ON THE ABSORPTION OF HYDROGEN CHLORIDE INTO VARIOUS ORGANIC LIQUIDS AND CALCULATION OF THE HEAT OF ABSORPTION. II.

By Senzo HAMAI.

Received March 4th, 1935. Published June 28th, 1935.

In a previous paper,[1] we published the results of the absorption of hydrogen chloride into various organic liquids such as 1,1,2,2-tetrachlorethane, ethylene chloride, carbon tetrachloride, and ethylene bromide, and also presented the purpose of this investigation along with necessary discussions in connection with it in detail. The present paper is a further report of similar measurements of the absorption of hydrogen chloride into several other organic liquids of the same series as the previous ones.

Experimental Procedure. The method of measuring the absorption of hydrogen chloride into these liquids is exactly the same as before and the apparatus remains essentially the same as that described previously except that the water-jacketed gas burette has been used with constant temperature water flowing in the jacket, and the measurements of the absorption have been carried out at 20°, 15°, and 12°C. and at various pressures.

Materials. Hydrogen chloride was prepared similarly as described in the previous report by dropping concentrated hydrochloric acid into pure concentrated sulphuric acid, passing the generated gas through two sulphuric acid bubblers, and condensing it twice by liquid nitrogen. Only the middle portion of it was used, after passed finally through a calcium chloride tube before it was allowed to fill the burette and reservoir.

1,1,2-Trichlorethane, b. p. 112.5°–113°C.[2] Eastman's product was distilled twice and once under reduced pressure.

Pentachlorethane, b.p. 158.5°–159.5°C.[2] Eastman's product was distilled twice and the constant boiling part was again distilled under reduced pressure.

(1) S. Hamai, this Bulletin, **10** (1935), 5.

(2) The boiling points of both liquids are somewhat lower than those given in the literature but they are distilled at essentially constant temperature.

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Results. The results of the absorption measurements with these organic liquids—the volume of hydrogen chloride absorbed per 20 c.c. of each liquid is reduced to the corresponding volume at 25°C.—are tabulated in Tables 1 and 2 with their corresponding molal fractions and mole percent.

The treatment of these results is exactly similar to that already published, namely the volume of hydrogen chloride absorbed is plotted against respective pressure at which the system finally reached an equilibrium, as shown, for an example, in Fig. 1 for 1,1,2-trichlorethane. The volume of hydrogen chloride to be absorbed at one atmosphere is obtained by extrapolation and this is converted into mole fraction and then the solubility of hydrogen chloride in respective liquids, i.e. N_{HCl} when P_{HCl} equals 760 mm., is obtained by assuming Henry's law is obeyed. In calculating the mole fractions for both liquids, the densities of the liquids at 20°, 15°, and 12°C. are obtained by interpolating those data given in Beilstein's Handbook. Table 3 shows N (20°, 15°, and 12°C.), $\log N$, and $(1/T) \times 10^{-3}$ and these are plotted in Fig. 2 and 3. ΔH for the heat of absorption can be calculated from

$$d \log N/d(1/T) = -\Delta H/(2.303 \times R).$$

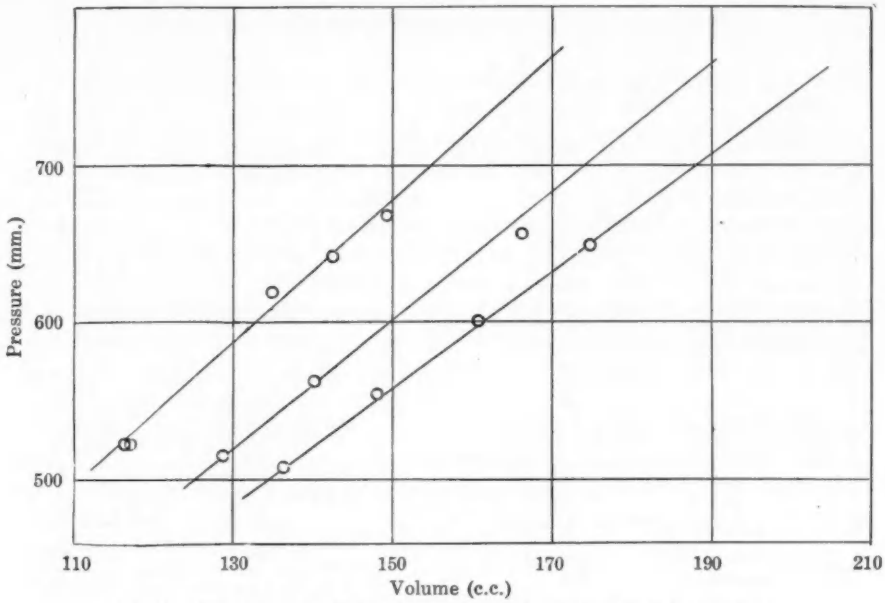
The values of ΔH thus found are also listed in Table 3.

Table 1. Absorption of Hydrogen chloride per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	620.0	134.33	0.02489	2.49
2	523.5	116.81	0.02171	2.17
3	667.0	149.57	0.02781	2.78
4	640.5	142.33	0.02633	2.63
5	620.0	134.24	0.02488	2.49
6	523.5	116.48	0.02166	2.17
		15°C.		
7	562.0	140.33	0.02688	2.59
8	516.0	128.70	0.02378	2.38
9	655.0	166.50	0.03056	3.06
		12°C.		
10	556.5	147.23	0.02705	2.71
11	649.0	174.77	0.03195	3.195
12	508.5	136.59	0.02514	2.51
13	601.5	160.11	0.02935	2.94

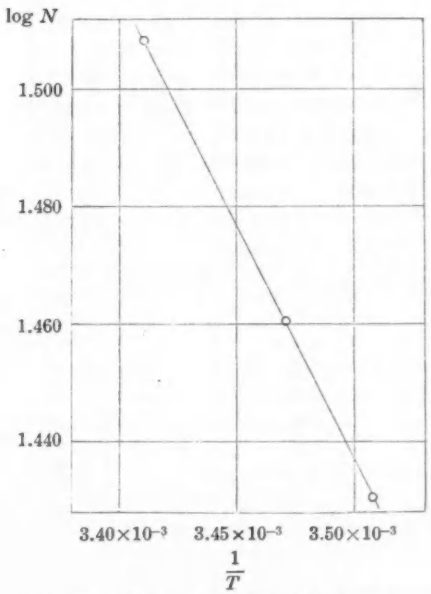
Table 2. Absorption of Hydrogen Chloride per 20 c.c. of Pentachlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	718.0	87.44	0.02125	2.13
2	565.5	68.25	0.01666	1.67
3	614.0	75.43	0.01838	1.84
4	666.0	79.58	0.01937	1.94
5	339.5	40.33	0.009946	0.995
		15°C.		
6	661.5	86.60	0.02096	2.10
7	611.5	79.76	0.01934	1.93
8	562.0	73.74	0.01790	1.79
9	661.5	86.60	0.02096	2.10
		12°C.		
10	712.5	98.90	0.02381	2.38
11	611.5	83.50	0.02018	2.02
12	560.5	76.86	0.01865	1.87
13	657.5	91.20	0.02199	2.20



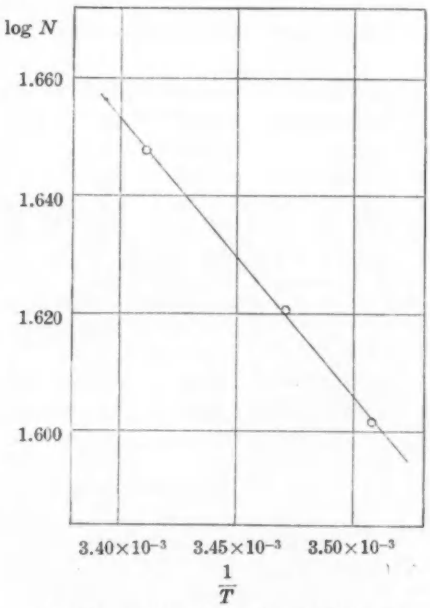
Volume of Hydrogen Chloride Absorbed per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C, and at Various Pressures.

Fig. 1.



Variation of the Absorption of Hydrogen Chloride into 1,1,2-Trichlorethane with Respect to Temperature.

Fig. 2.



Variation of the Absorption of Hydrogen Chloride into Pentachlorethane with Respect to Temperature.

Fig. 3.

Table 3.

Substance	N(HCl)	log N	$(1/T)\times10^{-3}$
20°C.			
1,1,2-Trichlorethane	0.03101	1.5085	3.411×10^{-3}
Pentachlorethane	0.02250	1.6478	,,
15°C.			
1,1,2-Trichlorethane	0.03463	1.46055	3.471×10^{-3}
Pentachlorethane	0.02396	1.6205	,,
12°C.			
1,1,2-Trichlorethane	0.03715	1.43004	3.508×10^{-3}
Pentachlorethane	0.02502	1.6017	,,

The Heat of Absorption ΔH/mole in cal.

	ΔH
1,1,2-Trichlorethane	3600 cal./mole
Pentachlorethane	2200 ,,

Table 5.

Bond	Bond energy	Substance	Total bond energy
C–Cl	3.22*v.e.	$C_2H_4Cl_2$	27.40 v.e.
C–Br	2.89*	$C_2H_4Br_2$	26.74 ,,
C–H	4.34	$C_2H_3Cl_3$	26.28 ,,
C–C	3.60	$C_2H_2Cl_4$	25.16 ,,
		C_2HCl_5	24.04 ,,
		CCl_4	12.88 ,,

Total Bond Energy

$C_2H_4Cl_2>C_2H_4Br_2>C_2H_3Cl_3>C_2H_2Cl_4>C_2HCl_5>CCl_4$

Solubility (N 20°C.)

$C_2H_4Cl_2>C_2H_4Br_2>C_2H_3Cl_3>C_2H_2Cl_4>C_2HCl_5>CCl_4$

* Average values of the various authors are used (A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56** (1934), 1096).

Table 4.

Substance	N(20°C.)	D.C.(20°)	$\mu\times10^{18}$	Mol. volume	Eötvös K	$T\frac{\alpha}{\beta}$	$E/V^{\frac{1}{3}}$
$ClCH_2{\cdot}CH_2Cl$	0.03993	10.8	1.8	78.90	2.15	4158	17.0
$BrCH_2{\cdot}CH_2Br$	0.03441	6.3	1.4	86.20	2.19	4455 4760	17.2
$Cl_2CH{\cdot}CH_2Cl$	0.03101	—	1.15*	92.31	2.21	—	—
$Cl_2CH{\cdot}CHCl_2$	0.02744	8.2	1.6	105.30	2.26	3362 3690	15.58
C_2HCl_5	0.02250	—	1.0*	120.59	2.32	—	—
CCl_4	0.01550	2.24	0.0	97.10	2.20	—	14.3

	Total bond energy	$(n-1)L/V$	$\frac{5200+30t_b}{V}$	Van Laar's a	$\gamma/V^{\frac{1}{3}}$	Sutherland	Mathews
$ClCH_2{\cdot}CH_2Cl$	27.40 v.e.	406	97.45	475	7.5	—	—
$BrCH_2{\cdot}CH_2Br$	26.74 ,,	422	105.23	549	8.7	710	3900
$Cl_2CH{\cdot}CH_2Cl$	26.28 ,,	—	93.05	335	—	—	—
$Cl_2CH{\cdot}CHCl_2$	25.16 ,,	368	90.72	555	7.71	—	—
C_2HCl_5	24.04 ,,	—	82.8	503	—	—	—
CCl_4	12.88 ,,	308	77.06	496	5.78	490	2660

* Van Arkel and Snock (unpublished) (C. P. Smyth, " Dielectric Constant and Molecular Structure ").

Discussion of Results. As we expected, the absorption of hydrogen chloride into 1,1,2-trichlorethane is much greater than into pentachlorethane as obvious from the tables; furthermore, by comparison with the data already published,[1] we find that the order of the solubilities in these various substances are not quite concordant with the order expected either from internal pressures as measured by various different methods or from polarities as indicated by several different ways, e.g. dielectric constant, electric moment, etc., as shown in Table 4, where the various quantities listed have significances as explained in our previous report. Also as already pointed out, we can hardly find any regularity with respect to molal volumes as well as Eötvös's K but they are well in the order of the total bond energies, as illustrated in Table 5.

Thus the solubilities of hydrogen chloride in these various halogen derivatives of the aliphatic hydrocarbon are not well accounted for either in the light of various criteria which are already considered elsewhere but they are well taken into account in the term of bond energies which have been more fully discussed in our previous paper.[1]

Summary.

(1) The absorption of hydrogen chloride into 1,1,2-trichlorethane and pentachlorethane at 20°; 15° and 12°C. has been measured.

(2) The heat of absorption of hydrogen chloride into these organic substances has been calculated.

(3) The order of the solubilities of hydrogen chloride into these liquids including those mentioned in our previous paper, is found to be well fitted in a scheme already described, namely they are in the order of the total bond energies of these substances.

In conclusion, the author wishes to express the best thanks to Prof. S. Mitsukuri for his kind advices and criticisms in the course of this investigation also hearty appreciation to generosity that a part of the expenses of this research has been covered by the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

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Correction to the previous paper (this volume, p. 5):

Read Ethyl bromide *for* Ethylene bromide *in Table 7 on page 13 and in line 2 on page 14.*

ON THE FATTY ACIDS OF JAPAN WAX.

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Received March 13th, 1935. Published June 28th, 1935.

The chemical composition of Japan wax (fruit-coat fat from the berries of "Hazé", *Rhus succedanea* L.) was chiefly investigated by foreign chemists and the specimens used by them were the bleached white wax. As the results of these researches Japan wax has been ascertained to consist mainly of tripalmitin and free palmitic acid. Besides them, of saturated acids small amounts of dibasic acids and of soluble acids (isobutyric?) were found. In some old books on fats and oils, stearic and arachidic acids were mentioned to occur in Japan wax. However, they could not be detected by A. C. Geitel and G. van der Want.[1] In the modern books, these acids, especially the latter, are usually omitted. Of unsaturated acids a small amount of oleic acid was stated to occur. Later Tassily[2] isolated pelargonic acid and an acid of the suggested formula $C_{15}H_{30}O_2$. Traces of stearic and oleic acids were also detected.

It is no wonder that oleic acid in Japan wax was rather neglected by foreign investigators, inasmuch as it is markedly changed or oxidised by the severe treatment of insolation on bleaching the wax. Also the presence of volatile or soluble acids is due to sun-bleaching process.

More than twenty years ago, the author[3] suggested the following composition of Japan wax fatty acids: palmitic acid 84%, oleic acid 14%, japanic acid(?) 2%. Nowadays the above amount of the dibasic acids has been found to be too small.[4]

The present experiments were made to reconfirm the components of the fatty acids (the dibasic acids being excepted) of genuine Japan wax. As the results the occurrence of stearic and arachidic acids has been ascertained, thus confirming the correctness of the description of the old books.

Experimental Part.

(1) **General Properties of the Specimen of Japan Wax.** The specimen used in this investigation was a raw or fresh wax, especially prepared from the berries

(1) *J. prakt. Chem.*, **61** (1900), 151.
(2) J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Vol. II (5th Edition), 654.
(3) *J. Soc. Chem. Ind. Japan*, **14** (1911), 321.
(4) Concerning the dibasic acids see M. Tsujimoto, this Bulletin, **6** (1931), 325.

("Komi"[5] or old berries) of *Rhus succedaneae* L. from the Prefecture of Kumamoto by the Higo Seirô Kaisha (Higo Wax Manufacturing Company), which contained no kernel oil.[6]

It was a brownish-yellow solid, which, though coherent and tenacious, was rather brittle. The characteristics, etc., were as follows:[7] Melt. pt. 53–53.5°C., d_4^{99} 0.8608, acid value 15.9, saponification value 208.1, iodine value 13.4, Reichert-Meissl value 0.38, unsaponifiable matter 0.77%.

As the specimen was free from the kernel oil, its iodine value was lower than those of commercial samples (iodine value, sometimes up to 20). The Reichert-Meissl value was very small indicating a negligible amount of volatile water-soluble acids.

The unsaponifiable matter was a brownish-yellow fine crystalline mass and produced a large amount of precipitate with digitonin in alcoholic solution.

The fatty acids formed a brownish-yellow crystalline mass of the following properties: Melt. pt. 63°C. (mainly liquefied at 61–62°C.), neutralisation value 215.3, iodine value 12.7, dibasic acids 6.3%.

The fatty acids were dissolved in acetone and on cooling the deposited solid acids were separated. By concentrating the filtrate, the crystallisation was repeated several times. The liquid acids were separated from the acids of the final filtrate by means of the lead-salt-ether method. They were of a brownish-yellow colour and had neutralisation value 193.1, iodine value 87.1, and n_D^{20} 1.4620. These figures nearly corresponded to those of oleic acid. On bromination in petroleum ether solution, they gave a small amount (ca. 1.7%) of a white precipitate; in ether solution, a little turbidity was observed, but nearly no precipitate. It appeared, therefore, that there occurred in the liquid acids a small proportion of linolic acid, but linolenic acid was almost absent in them.

(2) **Identification of the Component Fatty Acids.** The mixed fatty acids (unsaponifiable matter not removed) from the specimen of Japan wax were changed into methyl esters by boiling with half the weight of methanol containing 3% of H_2SO_4 upon a water bath for three hours. The ester mixture thus obtained was a brownish-yellow liquid in summer; it had still acid value 2.34, but was used without further treatment.

The methyl esters (1000 g.) were distilled (in batches of 250 g.) under 15 mm. pressure into the following fractions:

Fract.	Dist. temp.	Yield		Saponif. value	Iodine value	n_D^{20}
		(g.)	(%)			
I	Up to 200°	555.3	55.5	205.9	7.4	1.4389
II	200–205°	221.1	22.1	202.8	13.0	1.4395
III	205–210°	77.6	7.8	201.6	20.5	1.4410
IV	210–219°	60.2	6.0	198.7	32.1	1.4430

Distillates (total) 914.3 g. (91.4%). Residue 85.2 g. (8.5%)

(5) This Bulletin, **6** (1931), 326, foot-note.

(6) According to the author's experiments, the kernels of the berries of *Rhus succedanea* contained 4–9% of the oil. The oil had the following properties: d_4^{15} 0.9254–0.9289, acid value 2.16–4.32, saponification value 189.6–193.6, iodine value 125.2–133.2.

(7) All the iodine values were determined by Wijs method.

The residue consisted mainly of the methyl esters of the dibasic acids and the unsaponifiable matter.

The fractions were re-distilled under 15 mm. pressure. The results corresponding to 950 g. of the original esters were as follows:[8]

Fract.	Dist. temp.	Yield (g.)	Yield (%)	Appearance (at 20°C.)	Saponif. value	Iodine value	n_D^{20}
1	Up to 190°	0.7	0.07	White crystals	204.3	—	1.4375
2	190–200°	632.7	66.6	,,	205.0	6.2	1.4380
3	200–205°	120.6	12.7	White crystals and a little liquid	200.6	19.0	1.4400
4	205–210°	56.0	5.9	Nearly colourless liquid	198.6	26.7	1.4415
5	210–215°	23.8	2.5	,,	195.7	36.9	1.4431
6	215–222°	22.4	2.4	Pale yellow liquid	193.6	42.9	1.4450

Distillates (total) 856.2 g. (90.1%). Residue (brownish-yellow, crystalline mass) 11.0 g. (1.2%).

The distillation temperature soon rose above 180°C. The residue of the first fractionation was not re-distilled.

The fractions, especially the higher-boiling ones, showed notable unsaturation; this was apparently due to the methyl ester of oleic acid.

Each fraction was then examined for its component fatty acids.

Fraction 1 (up to 190°C./15 mm.). The yield was very small. Judged from its boiling point and saponification value, myristic acid and the lower homologues appeared not to be present. The free acid obtained from it, when crystallised from 90% alcohol, melted at 63°C., and by mixed test, was identified to be palmitic acid.

Fraction 2 (190–200°C./15 mm.). This was the principal constituent of the esters. To separate the solid part, 600 g. of the fraction was dissolved in about twice of its volume of acetone and well cooled with ice; the deposited solid was separated by a suction funnel. From the filtrate the acetone was distilled, and the remaining substance was again treated similarly. By these treatments 388 g. of a solid substance was obtained. It formed a beautiful, white crystals of m.p. 29°C., saponification value 206.7 and iodine value 0.64. Although it contained a very small amount of unsaturated substance, its properties nearly coincided with those of methyl palmitate (m.p. 30°C., saponif. value 207.6). The free acid obtained from it by saponification, on crystallising from alcohol, melted at 62°C. and had neutralisation value 218.7. So it consisted of palmitic acid (m.p. 62.6°C., neutr. value 218.9).

From the acetone-filtrate the solvent was distilled off, and on saponifying the remaining esters, 196. g. of fatty acids comparatively rich in liquid components were obtained. These were dissolved in four times of their volume of acetone, and kept at 18–20°C. overnight; the deposited solid was separated and the filtrate was again treated similarly.

(8) Though not strictly accurate, the following procedure was adopted. A fraction was distilled to a prescribed temperature and the residue was mixed to the next fraction and distilled; the distillate coming over to the temperature was mixed to the former fraction.

Such treatment was repeated several times, finally by cooling with ice. As the result, 170 g. of solid acids and 25 g. of crude liquid acids were obtained.

The solid acids melted at 60–60.5°C. and had neutralisation value 212.3 and iodine value 7.8. By crystallising the acids from alcohol, palmitic acid was isolated.

The crude liquid acids had iodine value 73.7 and were still admixed with solids. They were dissolved in 250 c.c. of 95% alcohol, and while hot, 5 g. of lead acetate was added to complete solution. On keeping at room temperature (18°C.) for five hours, the precipitate was filtered off, and on decomposing the insoluble and soluble lead salts, 5.8 g. of solid acids and 18.5 g. of liquid acids were obtained.

The solid acids had neutralisation value 203.4 and iodine value 53.9; so they contained more than half of the weight of unsaturated acids. On crystallisation from alcohol, the crystals melted at 52–52.5°C. By mixed test the chief component appeared to be palmitic acid.

The liquid acids were of an orange-yellow colour and had neutralisation value 194.7, iodine value 86.5, and n_D^{20} 1.4590. They were changed into methyl esters, and 18 g. of the esters were fractionally distilled under ca. 15 mm. pressure. The results were as follows:

Fract.	Dist. temp.	Yield (g.)	Appearance	Saponif. value	Iodine value	n_D^{20}
a	Up to 200°	0.5	Pale yellow liquid	179.9	70.5	1.4500
b	200–210°	10.8	,, ,, ,,	189.5	79.6	1.4520
c	210–216°	5.5	Light yellow liquid	187.8	83.9	1.4520

Residue (brownish-yellow liquid) 0.5 g.

The amount of fraction a was very small; its low saponification value was caused by the admixture of the remaining solvent. The fatty acids from this fraction had neutralisation value 193.5.

The saponification and iodine values of fractions b and c nearly corresponded to those of methyl oleate (saponif. value 189.3, iodine value 85.7). By the elaidin test (Hg and HNO_3), the free acids from these fractions solidified easily and gave elaidic acid of m.p. 44–44.5°C. The acids consisted, therefore, mainly of oleic acid. Hexadecenoic acid, $C_{16}H_{30}O_2$, did not appeared to occur in the present specimen of Japan wax. The presence of the oleic ester in the comparatively low-boiling fraction was due to the fact that a small amount of it was carried over with a large amount of methyl palmitate in the distillation.

Fraction 3 (200–205°C./15 mm.). On saponification, 111.7 g. of the fatty acids were obtained from 117 g. of this fraction. They were treated with acetone and then separated into solid and liquid acids by the lead-salt-alcohol method in the similar manner as described in the case of the previous fraction. Thus the acids were separated as follows:

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (A) deposited from acetone	97	209.3	12.0
,, ,, (B) obtained by lead-salt-alcohol method	4.6	206.5	32.3
Liquid acids ,, ,, ,,	10	197.7	84.8

On crystallising solid acids A from 90% alcohol, crystals of m.p. 60–60.5°C. were obtained; by mixed test they were identified to be palmitic acid. Solid acids B melted, after second recrystallisation, at 53–53.5°C.; the main component of their saturated acids consisted also of palmitic acid. By the elaidin test, the liquid acids were confirmed to consist mainly of oleic acid.

Fraction 4 (205–210°C./15 mm.). The fraction (54 g.) gave 51.4 g. of the fatty acids, which were treated similarly as previously described.

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (C) deposited from acetone	38	207.1	14.6
,, ,, (D) obtained by lead-salt-alcohol method	4.7	208.3	37.1
Liquid acids ,, ,, ,,	8.1	196.6	87.6

Solid acids C, when recrystallised from 90% alcohol, melted at 55°C.; the high boiling point of the fraction indicated the presence of some saturated acids (possibly stearic acid) higher than palmitic acid. Solid acids D melted, after recrystallisation, at 53°C.; they appeared still to contain palmitic acid. The liquid acids consisted mostly of oleic acid.

Fraction 5 (210–215°C./15 mm.). This fraction was mostly liquid at 15°C., though a notable amount of crystals was deposited. On saponification 20.9 g. of the fatty acids were obtained from 22 g. of the fraction. They were dissolved in 70% acetone and cooled with ice; the deposited solid acids were separated from the solution. The fatty acids remaining on evaporating off the acetone were then dissolved in 100 c.c. of 95% alcohol, and the still admixed solid acids were precipitated by adding 1 g. of lead acetate. By these procedures the following results were obtained:

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (E) deposited from acetone	12.6	51–52°	206.0	12.0	—
Solid acids (F) obtained by lead-salt-alcohol method	1.2	61°	213.1	23.5	—
Liquid acids ,, ,, ,, ,,	7.1	—	198.7	85.6	1.4600

Solid acids E (10 g.) were dissolved in 300 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate as follows:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.9	57 – 57.5°C.	201.2
,, ,, ,, 2nd ,,	1.9	54.5–55°C.	205.2
,, ,, ,, 3rd ,,	1.8	54 - 54.5°C.	208.4
,, ,, ,, 4th ,,	1.9	54 – 54.5°C.	212.7
,, ,, ,, 5th ,,	1.5	57 – 57.5°C.	212.8

As the above results show, besides palmitic acid, the presence of stearic acid in the acids would be expected. By fractionally precipitating the fatty acids from the 1st precipitate, 0.3 g. of a solid of m.p. 61.5–62°C. and neutralisation value 189.9 was obtained. Judged from the neutralisation value, this substance appeared to be a mixture of stearic and the higher saturated acids.

Solid acids F contained a fairly large amount of unsaturated acids; as the neutralisation value was high, their main component was probably palmitic acid.

The liquid acids readily formed elaidic acid (m.p. 43.5–44°C.), so the main component was oleic acid.

Fraction 6 (215–222°C./15 mm.). This fraction formed a soft crystalline mass at 15°C. It (20 g.) gave 19.3 g. of the fatty acids, which were treated in the same way as those of preceding fraction.

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (G) deposited from acetone	8.1	64°C. (mainly liquid at 60°C.)	202.5	0.8	—
Solid acids (H) obtained by lead-salt-alcohol method	2.6	52°C.	213.2	37.4	—
Liquid acids „ „ „ „	8.3	—	195.2	86.2	1.4600

The solid acids G consisted mostly of saturated acids. As they were found to contain a small amount of the dibasic acids, 7.8 g. of them were dissolved in about 50 times of their volume of petroleum ether in the hot and kept at room temperature of 22–25°C; the deposited dibasic acids (0.4 g.) were then filtered off.

The acids (6.5 g.) thus freed from the dibasic acids were dissolved in 200 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate.

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.5	61 – 61.5°C.	192.3
„ „ „ 2nd „	1.5	60 – 60.5°C.	195.8
„ „ „ 3rd „	1.8	60.5–61°C.	202.1
„ „ „ 4th „	1.3	55 – 55.5°C.	208.8

The last mother liquor gave, on evaporation, a soft crystalline mass.

The fatty acids from the 1st and 2nd precipitates were mixed and repeatedly recrystallised from alcohol with the following results:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st recrystallisation	1.4	63°C.	—
„ „ „ 2nd „	0.8	64.5–65°C.	—
„ „ „ 3rd „	0.4	70 – 70.5°C.	183.5

The last acids, when mixed with an equal part of arachidic acid (m.p. of the specimen 75°C.), melted at 72–72.5°C. On analysis the substance gave the following results: Found: C, 76.80; H, 13.06. Calc. for $C_{20}H_{40}O_2$: C, 76.84; H, 12.91%. The substance was, therefore, confirmed to be somewhat impure arachidic acid (m.p. 77°C., neutr. value 179.6).

The mother liquor of the arachidic acid was twice concentrated, the deposited solid (yield ca. 1 g.) separated, and on further concentration 0.45 g. of crystals was obtained.

This substance melted at 63–64°C. and had neutralisation value 194.0; mixed with stearic acid (equal part) it melted at 66–66.5°C. Found: C, 75.44; H, 12.93. Calc. for $C_{18}H_{36}O_2$: C, 75.98; H, 12.76%. Thus the substance consisted of stearic acid.

The acids intermediately deposited (neutr. value 188.3 and 193.5) were mixtures of arachidic and stearic acids.

The fatty acids from the 4th precipitate appeared to be a mixture of stearic and palmitic acids.

The solid acids H contained a notable amount of unsaturated acids; on crystallising them from 90% alcohol, crystals having m.p. 57–58°C. and neutralisation value 212.2 were obtained, so they consisted mainly of palmitic acid. It was rather unexpected to find the presence of palmitic acid in such a high-boiling fraction, though the amount was very small; this indicated the difficulty of thoroughly separating fatty acids from one another by simple fractional distillation of their methyl esters.

The liquid acids formed elaidic acid of m.p. 43.5°C., so they were identified to be oleic acid.

The distillation residue of the second fractionation of the original esters consisted mainly of the esters of the dibasic acids. It should be noted that notwithstanding their high boiling points these esters distilled over together with those of the fatty acids, but their amount was comparatively small.

(3) **On the Free Fatty Acids in Japan Wax.** The amounts of free acids in commercial samples of Japan wax vary somewhat markedly and are usually rather high, but the unbleached wax contains a far smaller amount than the sun-bleached one. The following brief experiment was performed to ascertain the components of the free acids.

The specimen of Japan wax (50 g.) was heated with 200 c.c. of 90% alcohol to dissolve out the free acids; on cooling the wax sank and solidified, hereupon the upper solution was decanted. The wax was again treated with 100 c.c. of alcohol. The alcoholic solutions, which deposited notable amounts of solids, were united, neutralised with alcoholic NaOH solution, and evaporated to dryness. The solid residue was mixed with sand and extracted with petroleum ether in a Soxhlet apparatus to remove neutral wax. The soap was then decomposed with diluted hydrochloric acid.

The free acids thus separated amounted to 2.7 g. They formed a pale brownish-yellow solid, and had neutralisation value 195.4, saponification value 212.9, and iodine value 26.7; the content of the dibasic acids was 5.1%. A further treatment of the extraction of neutral wax was made to ensure the complete removal of it. Then the acids had neutralisation value 206.2 and iodine value 27.1.

From the above results, it has been concluded that the components of the free acids were nearly the same as the mixed acids of the wax, but oleic acid was present in a far larger proportion.

Summary.

The component fatty acids of a specimen of unbleached Japan wax, which contains no kernel oil, have been examined.

In agreement with the description in fat literature, palmitic acid is, of course, the main component. Myristic acid and the lower homologues appear not to be present; volatile lower acids stated to occur in Japan wax by old investigators are undoubtedly decomposition products formed by bleaching process. On the other hand, stearic and arachidic acids occur in appreciable proportions. The unsaturated acids consist mostly of oleic acid. A small proportion of linolic acid is present. Hexadecenoic and linolenic acids are probably not present.

It is difficult to mention the quantitative proportion of the individual acids, but rough approximation would be as follows: Palmitic acid 77%, stearic and arachidic acids 5%, oleic acid 12%, linolic acid small amount (less than 1%), dibasic acids 6%.

The above proportion of stearic and arachidic acids would be rather high; in their relative amounts the former seems to predominate.

It is interesting to observe that whereas myristic acid can not be detected in Japan wax obtained from *Rhus succedanea*, it occurs abundantly in the wax of "Tsutaurushi", *Rhus toxicodendron, var. vulgaris*, a viny shrub belonging to the same genus *Rhus*.[9]

The free acids in Japan wax have nearly the same composition as the mixed acids of the wax, but oleic acid is present in a far larger proportion.

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(9) This Bulletin, **6** (1931), 340, foot-note.

STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. PART IV. RAMAN EFFECT OF CEDRENE.

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Received March 22nd, 1935. Published June 28th, 1935.

Introduction.

In the present paper, the Raman effect of cedrene is reported, the constitution of which has been studied by Prof. K. Kafuku[1] and others[2] on the standpoint of the organic chemistry. The result of the Raman effect in the present investigation seems to provide an evidence for the organic chemists' idea regarding the constitution. The further discussion will be reported after studying the Raman spectra of the derivatives of cedrene and other terpenes, which are in the course of experiments.

Experimental.

The so-called "artificial cedrene" (b.p. 116–118°/10 mm., n_D^{30} 1.494) obtained by the dehydration of cedrol, was kindly supplied by Ass. Prof. T. Nozoe and Mr. K. Kuraoka. The Raman spectrum of this sample was taken by means of a spectrograph with two prisms. Six hours' exposure was enough for obtaining an intense Raman spectrum (Plate 1) in the total region of the visible part. The experiments were repeated by using a new sample obtained by dehydrating cedrol (m.p. 86°) supplied by Dr. Ichikawa of the Central Research Institute of Formosa. Using this new sample of cedrene, the Raman spectrum was obtained with a spectrograph of three prisms[3] by using a saturated solution of sodium nitrite as a filter (Plate 2). A longer exposure of 12–14 hours was required in this case. No difference was found in the above-mentioned two results. The data of the Raman spectrum are shown in Table I.

For the purification, the substances were dehydrated over calcium chloride, and then redistilled over metallic sodium in vacuum (b.p. 116–117°/10 mm., n_D^{30} 1.4943).

(1) K. Kafuku, *J. Chem. Soc. Japan*, **55** (1934), 1235.
(2) Simonsen, "The Terpenes", Vol. II (1932), p. 530.
(3) This Bulletin, **9** (1934), 327.

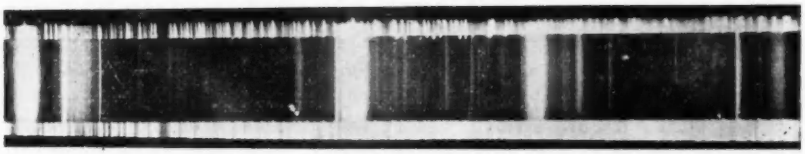


Plate 1. Raman Spectrum of Cedrene (I)

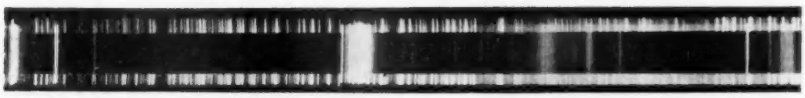


Plate 2. Raman Spectrum of Cedrene (II)

Table I. Raman Spectrum of Cedrene.

No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)
1	24560	4	q-2828(k-145)	25	23885	3	k- 820(i-631)
2	24525	½(d)	p-2828(k-180)	26	23855	2(d)	k- 850(i-661)
3	24474	4(d)	q-2914(k-231)	27	23787	2(b, d)	k- 918
4	24443	5(d)	k- 262(p-2910)	28	23763	3(d)	k- 942
5	24418	5(d)	q-2970	29	23737	2	k- 968
6	24391	5(b)	k- 314	30	23704	3(d)	k-1001
7	24381	½	p-2972	31	23680	½	k-1025
8	24362	½	k- 343(q-3026)	32	23666	3(b, d)	k-1039(i-850)
9	24314	2(b)	k- 391	33	23637	3(d)	k-1068
10	24293	1(b)	k- 412	34	23601	2	k-1104
11	24269	2(b, d)	k- 436	35	23579	4(b)	k-1126(i-937)
12	24250	2(b)	k- 455	36	23563	4(b)	k-1142
13	24211	2	k- 494	37	23537	3(b, d)	k-1168
14	24171	3	k- 534	38	23503	2	k-1202
15	24131	5	k- 574	39	23485	3(d)	k-1220
16	24116	2	k- 589	40	23465	3(d)	k-1240
17	24092	2	k- 613	41	23432	4	k-1273(i-1084)
18	24073	½	k- 632	42	23404	2	k-1301
19	24048	2	k- 657	43	23385 ?	0	k-1320
20	24006	2	k- 699	44	23354	4	k-1351
21	23973	5(d)	k- 732	45	23330	4	k-1375
22	23942	½	i- 574	46	23295	½(d)	i-1221
23	23925	5	k- 780(i-591)	47	23271	6	k-1434
24	23905	½	k- 800(i-611)	48	23257	6(b, d)	k-1448

Table I. (*Concluded*)

No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)
49	23251	6(b, d)	k-1454	85	22088	4(b, d)	e- 850(f-907)
50	23228	3(d)	k-1477	86	22065	½(d)	f- 930(e-873)
51	23195	2(d)	e+257	87	22026	5(b, d)	e- 912
52	23124	2(d)	e+186	88	22001	6 b, d)	e- 937
53	23080	3(b)	i-1436(e+142)	89	21973	5(b, d)	e- 965
54	23039	?	k-1666(hg)	90	21952	3(d)	e- 986?(f-1043)
55	22851	2(b, d)	e- 87	91	21937	5(d)	e-1001
56	22814 ?	0(d)	e- 124	92	21914	2	e-1024
57	22794	4(bb, d)	e- 144	93	21901	3	e-1037
58	22749	3(b, d)	e- 189	94	21874	6	e-1064(f-1121)
59	22701	½(d)	e- 237	95	21851	2	e-1087?(f-1144)
60	22680	4(b, d)	e- 258(f-315)	96	21831	6(d)	e-1107(k-2874)
61	22650	0	e- 288	97	21811	5(b)	e-1127
62	22630	4	e- 308	98	21795	6(b)	e-1143 (k-2914, f-1200)
63	22621	3	e- 317				
64	22598	1	e- 340	99	21771	6(b)	e-1167(k-2934)
65	22574	2	e- 364	100	21737	6(b)	e-1201(k-2968)
66	22549	3(b, d)	e- 389	101	21719	2	e-1219
67	22528	3	e- 410	102	21704	3(b, d)	e-1234
68	22501	2(d)	e- 437	103	21669	2(d)	k-3036
69	22485	2(d)	e- 453	104	21660	5	e-1278
70	22469	0(d)	f- 526	105	21641	5	e-1297(f-1354)
71	22447	3	e- 491	106	21608	2 dd)	e-1330
72	22406	5	e- 532	107	21588	5	e-1350
73	22388	½	e- 550(f-607)	108	21563	5	e-1375(f-1432)
74	22367	8	e- 571(f-628)	109	21504	8	e-1434
75	22351	4	e- 587	110	21486	8	e-1452
76	22327	4	e- 611	111	21465	6(bb)	e-1473
77	22308	2	e- 630	112	21292	½	e-1646
78	22282	3	e- 656	113	21272	10	e-1666
79	22240	3	e- 698	114	21106	2(b)	e-2832
80	22205	8(b, d)	e- 733	115	20063	2	e-2875(f-2932)
81	22158	8	e- 780	116	20020	6(b, d)	e-2918
82	22136	2	e- 802	117	19999	6(b)	e-2939
83	22119	6	e- 819	118	19971	6(d)	e-2967(f-3024)
84	22105	½	e- 833	119	19914	2(d)	e-3024

$\Delta\nu$: (87) (2b, d); (124) (0d) ?; 144 (4bb, d); 189 (3b, d); 237 (½d); 260 (4b, d); (288) (0); 308 (4); 317 (3); 340 (1); (364) (2); 389 (3b, d); 410 (3); 437 (2d); 454 (2d); 491 (3); 532 (5); (550) (½) ?; 571 (8); 587 (4); 611 (4); 630 (2); 656 (3); 698 (3); 733 (8b, d); 780 (8); 802 (2); 819 (6); (833) (½); 850 (4b, d); (873) (½d) ?; 915 (5b, d); 938 (6b, d); 965 (5b, d); (986) (3d) ?; 1001 (5d); 1024 (2); 1038 (3); 1066 (6); (1087) (2) ?; 1105 (2d); 1127 (5b); 1143 (6b); 1167 (6b); 1201 (6b); 1219 (2); 1237 (3b, d); 1275 (5); 1297 (5); 1325 (2dd); 1350 (5); 1375 (5); 1434 (8); 1452 (8); 1475 (6b, d); (1646) (½) ?; 1666 (10); 2830 (2b); 2875 (2); 3030 (2d); 2916 (6b, d); 2937 (6b); 2967 (6b)

Discussion.

The Raman spectrum of cedrene is the most complicated one. It contains one-hundred-nineteen lines. And some of the Raman lines are

observed at the equal intervals. The mean interval between them is 25 cm.$^{-1}$, as shown below:

317		1101		1325	
	23		26		25
340		1127		1350	
	24				25
364		1143		1375	
	25		24		
389		1167			
	21				
410		1271			
	27		26		
437		1297			

According to the usual estimation, the lower frequencies may be ascribed to the deformation of the carbon linkages. And when we put

$$\omega_1 = 144,\quad \omega_2 = 308,\quad \omega_3 = 317,\quad \omega_4 = 364,\quad \omega_5 = 389,\quad \omega_6 = 410,\quad \omega_7 = 437,$$
$$\omega_8 = 454,\quad \omega_9 = 491,\quad \omega_{10} = 532,\quad \omega_{11} = (550),\quad \omega_{12} = 571,\quad \omega_{13} = 587,\quad \omega_{14} = 611,$$

we find that a number of the Raman lines higher than $\Delta\nu$ 630 cm.$^{-1}$ are two times as great as the above-mentioned frequencies as shown in Table II. These lines may be taken as the overtone of the corresponding lower ones.

Table II. The Frequencies Associated with the Overtone.

$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$	$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$
$2\omega_1 = 288$	(288)(0)	0	$2\omega_8 = 908$	915 (5b, d)	-7
$2\omega_2 = 616$	611 (4)	5	$2\omega_9 = 982$	(986)(3d) ?	-4
$2\omega_3 = 634$	630 (2)	4	$2\omega_{10} = 1064$	1066 (6)	-2
$2\omega_4 = 728$	733 (8)	-5	$2\omega_{11} = 1100$	1105 (2d)	-1
$2\omega_5 = 778$	780 (8)	-2	$2\omega_{12} = 1142$	1143 (6b)	-1
$2\omega_6 = 820$	819 (6)	1	$2\omega_{13} = 1174$	1167 (6b)	7
$2\omega_7 = 874$	(873)($\frac{1}{2}$)	1	$2\omega_{14} = 1222$	1219 (2)	3

From the result compared in Table II, it seems to be impossible to assign the intense lines of $\Delta\nu$ 733(8), 780(8), 915(5b, d), 1066(6), 1143(6b), and 1167(6b), simply as the overtone of the above-mentioned frequencies. Another origin must be taken into consideration.

As the usual assignment, the frequencies in the region of $\Delta\nu$ 733–1066 cm.$^{-1}$ may be attributable to the valency frequencies of the C–C bond. It will be noted that the organic chemists' picture[4] of the molecule indicates that:

(4) Cf. (2).

(1) Cedrene is a tricyclic compound.

(2) There are carbon atoms holding one, two, three, and none hydrogen atoms, that is, $\begin{matrix} & C & \\ & | & \\ C-&CH&- \\ & | & \\ & C & \end{matrix}$, $-CH_2-$, $-CH_3$ and $\begin{matrix} & C & \\ & | & \\ C-&C&-C \\ & | & \\ & C & \end{matrix}$.

(3) The molecule includes more possibly a 1-methyl-cyclopentene-(1) than a 1-methyl-cyclohexene-(1) ring.

From these points of view, let us compare, in the first place, the Raman spectrum of cedrene with those of the other simple paraffine molecules which have been observed by Kohlrausch and Köppl[5]. As shown in Table III, in the paraffine series, the frequencies of ca. $\Delta\nu$ 840 and 890 cm.$^{-1}$ are found in the normal compounds, while the corresponding shifts in their isomerides are ca. $\Delta\nu$ 780 and 950 cm.$^{-1}$. It is also found that $\Delta\nu$ 1335 cm.$^{-1}$ disappears in the normal compounds, and $\Delta\nu$ 1066 cm.$^{-1}$ does in the iso-compounds.

Table III. Raman Frequencies of the Normal- and Iso-Praffines.

C_nH_{2n+2}	a	b	c	d	e	f	g	h	i	j	k	l
C_4H_{10} (*n*)	298	—	825	(873)	895	—	1058	1006	—	1299	—	1447
C_5H_{12} (*n*)	—	—	841		895	1027	1066	1110	—	1301	—	1446
C_6H_{14} (*n*)	269	—	822	863	889	1026	1069	1112	—	1302	—	1446
C_7H_{16} (*n*)	256	—	845		886	1021	1069	1113	1169	1300	—	1445
C_4H_{10} (*i*)	335	427	(789)	832	954	(1029)	—	1120	1168	1298	1334	1454
C_5H_{12} (*i*)	(366)	424	773	826	953	(1030)	—	1123	1167	(1295)	1337	1453

In the second place, let us consider the Raman spectrum of tetramethyl-methane which was studied by the above authors[7] and Rank.[6] Kohlrausch and Köppl[7] have ascribed ω_1 732(10), ω_2 332(4b), ω_3 921 (7b), and ω_4 416(1) in tetramethyl-methane to the vibration frequencies of the $\begin{matrix} & C & \\ & | & \\ C-&C&-C \\ & | & \\ & C & \end{matrix}$ linkage, while ω_1 795(9), ω_2 371(4b), ω_3 965(4b) and ω_4 437(1) in iso-butane to the $C-\left(\begin{matrix} C \\ | \\ CH \\ | \\ C \end{matrix}\right)$ linkage. From the fact that

(5) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **24** (1934), 377.

(6) D. H. Rank, *J. Chem. Phys.*, **1**, (1933), 572.

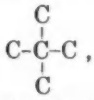
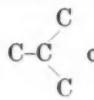
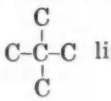
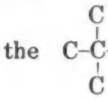
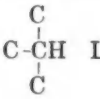
the above-mentioned Raman lines are also observed in the other isomerides of paraffines and their derivatives having the valency bond of or  , as shown in Table IV, and the fact of the disappearance and the displacement of the frequencies in the normal compounds of the paraffine series as shown in Table III, we may ascribe the frequencies in the regions of 732–795 and 915–965 cm.$^{-1}$ to the valency frequencies of the  or  linkage.

Table IV. Raman Frequencies Possibly Associated with the  or  Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Tetramethyl-methane[7]	732 (10)	333 (4b)	921 (7b)	416 (1)
Tertiary butylcarbinol[8]	744 (9)	333 (2b) 350 (2b)	933 (4)	407 ($\frac{1}{2}$)
Tertiary amylcarbinol[8]	714 (4) 726 (3)	350 (2)	903 (2) 931 (2)	405 (0) 441 ($\frac{1}{2}$)
Isobutane[7]	795 (9)	371 (4b)	965 (4b)	437 (1)
Isopentane[9]	762 (5) 796 (4)	366 (1)	906 (2) 948 (2)	469 (4)
Isobutyl alcohol[9]	782 (2)	361 ($\frac{1}{2}$)	953 (3b)	494 (4)
Isobutyl amine[9]	792 (5b)	363 (2b)	952 (3)	480 (4b)
Methyl-isopropylcarbinol[8]	757 (2b) 786 (3)	358 (1)	930 (3) 954 (2)	462 ($\frac{1}{2}$) 496 ($\frac{1}{2}$)
2,5-Dimethyl-hexane[10]	778 (2)	313 (2)	962 (3br)	444 (4b)

(7) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **26** (1934), 219.
(8) K. W. F. Kohlrausch and F. Köppl, *Monatsh.*, **63** (1933), 269.
(9) H. Kopper, R. Seka and K. W. F. Kohlrausch, *Monatsh.*, **61** (1932), 403.
(10) John W. Murry, *J. Chem. Phys.*, **2** (1934), 618.

Table V. The Vibration Frequencies Associated with the C(C)(C)–C or C(C)–CH(C) Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Isobutane	785 (9)	371 (4b)	965 (4b)	437 (1)
Cedrene	780 (8) 733 (8)	389 (3b, d) 317 (3)	965 (5b) 915 (5b, d)	427 (2d) 410 (3)
Tetramethyl-methane	732 (10)	332 (4b)	921 (7b)	416 (1)

Table VI. The Valency Frequencies of the Carbon Bonds.

Cedrene	α-Pinene		β-Pinene[12]	Sabinene[13]
	V.B.[11]	M.H.[13]		
733 (8)	—	—	—	729 (1d)
780 (8)	774 (2)	774 (6)	786 (5)	786 (5)
802 (2)	—	—	—	—
819 (5)	816 (0)	818 (2)	—	808 (4d)
850 (4b, d)	844 (2)	844 (7)	850 (5)	—
(873)(½)	878 (0)	885 (2)	879 (5)	882 (2d)
915 (5b, d)	904 (1)	908 (4)	—	916 (6d)
938 (6b, d)	931 (0)	933 (2)	—	930 (1)
965 (5b)	949 (3)	954 (5d)	942 (4)	953 (6b)
986 (3)	—	—	—	989 (3)

It may, therefore, be possible to assign the frequensies of $\Delta\nu$ 733, 780, 915, and 965 cm.$^{-1}$ in cedrene as due to these linkages in the cedrene molecule. The vibration frequencies associated with the linkage in question in cedrene are compared also with those in iso-butane and tetramethyl-methane as shown in Table V. It is interesting that the relation of the intensities of these lines in the latter are similar to that in the former. As to the other Raman lines in the region of 802–850 cm.$^{-1}$, they may be attributable to the $-CH_2-CH_2-$ linkage of the ring.

Further, let us compare the Raman lines which are possibly associated with the valency frequencies of the carbon linkages in cedrene with those

(11) S. Venkateswaran and S. Bhagavantam, *Ind. J. Phys.*, **7** (1933), 585.
(12) G. Dupont, P. Daure and J. Allard, *Bull. soc. chim.*, **49** (1932), 1401.
(13) The details will be published shortly in this Bulletin.

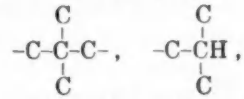
in the other terpenes, such as α-pinene, β-pinene, and sabinene, which have been known to have the carbon linkages of  , , $-CH_2-$ and $-CH_3$ (Table VI). The frequencies of $\Delta\nu$ 780, 873, and 965 cm.$^{-1}$ in cedrene are also found in α-pinene, β-pinene, and sabinene. The frequencies of $\Delta\nu$ 819, 915 and 938 cm.$^{-1}$ appear in cedrene, α-pinene, and sabinene, but not in β-pinene. The frequency of $\Delta\nu$ 850 cm.$^{-1}$ appears in cedrene, α-pinene, and β-pinene, but not in sabinene. The fact that all the shifts between $\Delta\nu$ 733 and 986 cm.$^{-1}$ in cedrene are found also in α-pinene, β-pinene, or sabinene seems to give a verification of the organic chemists' idea regarding the constitution of cedrene.

Table VII. Comparison of the Raman Frequencies in Cedrene, 1-Methyl-cyclopentene-(1) and 1-Methyl-cyclohexene-(1).

Methyl-cyclopentene (Godchot, etc.)[15]	Methyl-cyclopentene (Piaux)[16]	Cedrene	Methyl-cyclohexene (Godchot, etc.)[15]	Methyl-cyclopentene (Godchot, etc.)[15]	Methyl-cyclopentene (Piaux)[16]	Cedrene	Methyl-cyclohexene (Godchot, etc.)[15]
—	—	308	—	—	928	938	—
333	325	317	—	—	—	965	—
		340		—	—	(986)?	990
—	—	364	—	—	1008	1001	—
—	—	389	—	1017	1026	1024	—
—	—	410	—	—	—	1038	—
437	432	437	437	—	—	1066	1069
—	—	454	—	1083	—	(1087)?	1087
—	—	491	495	—	—	1105	—
—	—	532	—	—	1133	1127	—
578	578	571	—	—	1148	1143	1152
—	—	587	588	—	—	1167	—
—	—	611	618	—	1207	1201	—
—	—	630		—	—	1219	—
—	648	656	—	1278	1259	1275	1266
—	—	698	695	—	1295	1297	1309
—	—	733		1336	1333	1325	1367
—	790	780	758	—	—	1350	—
—	—	802	—	1385	1383	1375	—
—	821	819	821	1445	1439	1434	1445
—	851	850	859		1465	1452	
879	881	(873)?	—			1475	
—	903	915	—	1660	1658	1666	1675

(14) The details will be published shortly in this Bulletin.

(15) Marcet Godchot, Etienne Canales, and Germaine Cauquil, *Compt. rend.*, **197** (1933), 1408.

(16) Leon Piaux, *Compt. rend.*, **199** (1934), 67.

The facts that almost all the Raman lines observed in cyclohexane occur also in decahydro-naphthalene and decahydro-acenaphthene[14] and that many of the Raman lines of cedrene coinside with those of 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1) (Table VII) give an another evidence of the organic chemists' constitution of cedrene.

The most intense line at $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the inner vibration of the C=C bond. This frequency is generally influenced rather remarkably by the adjacent atoms or atom groups of the bond in the molecule. The frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is compared with that in the other molecules which have the C=C linkage, as shown in Table VIII.

From the results we may summarize that the Raman frequency due to the C=C linkage indicates a constant value for each type of the molecules. And by the substitution of a methyl or methylene group for a hydrogen atom attached to the double bond of the carbon atoms the frequency is increased about 20 cm.$^{-1}$, with an exception of cyclopentene in which it is increased about 40 cm.$^{-1}$, as shown below:

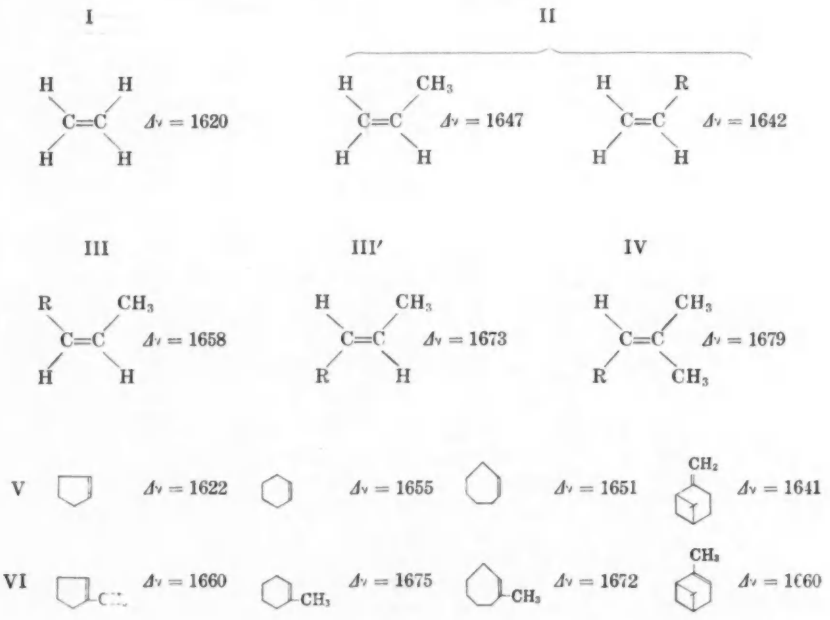
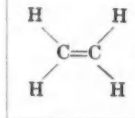
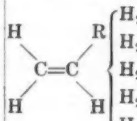
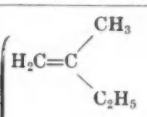
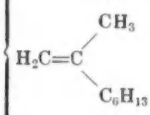
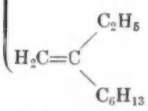
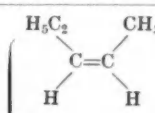
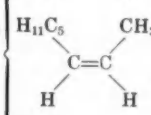
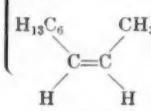
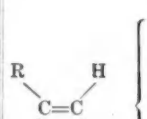
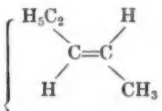
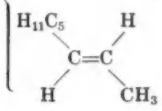
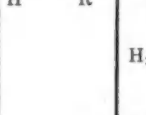
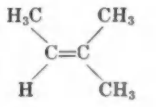
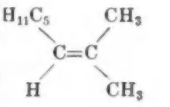
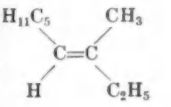
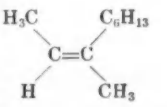
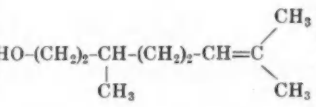


Table VIII. Raman Frequencies Associated with the C=C Bond.

	$H_2C{=}CH_2$	1620[17]	
	$H_2C{-}CH{-}CH_3$	1647[17]	
	$H_2C{-}CH{-}CH_2OH$	1646[17]	
	$H_2C{-}CH{-}CH_2Cl$	1640[17]	
	$H_2C{-}CH{-}CH_2{-}C_6H_5$	1642[17]	
	$H_2C{-}CH{-}C_nH_{2n+1}$ $(n=2-8)$	1642[17]	
		1652[19]	
		1647[18]	
		1646[18]	
		1658[20]	
		1658[20]	
		1658[20]	
		1674[20]	
		1673[20]	
		1679[21]	
		1677[18]	
		1670[18]	
		1672[18]	
		1675[27]	

(17) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 495.
(18) B. Gredy, *Compt. rend.*, **195** (1932), 313.
(19) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 480.
(20) M. Bourguel, B. Gredy, and L. Piaux, *Compt. rend.*, **195** (1932), 129.
(21) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 474.

Table VIII. (*Concluded*)

	1622[22]		1655[22]		1651[22]		
	1660[23]		1650[23]		1672[23]		1660[25]
	1660[23]		1675[23]				
	1656[24]		1675[23]				1641[26]
			1680[23]				
			1677[23]				

Table IX. The Raman Frequencies Associated with the $-C=\overset{\overset{CH_3}{|}}{C}-$ Linkage.

Butadiene[28]	—	Geraniol[29]	1388
1-Methyl-butadiene[28]	1370	Linalool[30]	1383
Isoprene[28]	1380	Carvone[31]	1378
2,3-Dimethyl-butadiene[28]	1377	Pulegone[32]	1379
Phenyl-ethylene[28]	—	Cyclopentene[22]	—
Phenyl-methyl-ethylene[28]	1376	1-Methyl-cyclopentene-(1)[23]	1385
Chloroprophylene[28]	1375	Cyclohexene[22]	—
Methyl crotonate[28]	1375	1-Methyl-cyclohexene-(1)[22]	1367
Methyl iso-crotonate[29]	1367	Cycloheptene[22]	—
Crotonic acid[28]	1381	1-Methyl-heptene-(1)[23]	1379
α-Pinene[25]	1383	Octene[22]	—
β-Pinene[26]	—		

From these results, we may conclude that the most intense line corresponding to the frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the C=C bond in the type of $H_{20}C_{12}\diagdown\overset{\overset{CH}{\|}}{C-CH_3}\diagup$, as described by the organic chemists. By comparing with the corresponding Raman

(22) M. Godchot, etc., *Compt. rend.*, **196** (1933), 780.
(23) M. Godchot, etc., *ibid.*, **197** (1933), 1407.
(24) L. Piaux, *ibid.*, **199** (1934), 67.
(25) Cf. (13).
(26) Cf. (12).
(27) G. B. Bonino, and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 20.
(28) Kohlrausch, "Smekal-Raman-Effekt", (1931), p. 322–327.
(29) G. B. Bonino and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 22.
(30) *Ibid.*, p. 21. (31) *Ibid.*, p. 8. (32) *Ibid.*, p. 6.

shift in 1-methyl-cyclopentene-(1) ($\Delta\nu$ 1660 cm.$^{-1}$) and 1-methyl-cyclohexene-(1) ($\Delta\nu$ 1675 cm.$^{-1}$), it seems that the frequency in question appears more likely in the case of 1-methyl-cyclopentene-(1) than in the case of 1-methyl-cyclohexene-(1). The difference is, however, too small to distinguish the latter from the former, as the frequency $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is situated between the frequencies in 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1). That is: $\Delta\nu$ 1660 cm.$^{-1}$; cedrene $\Delta\nu$ 1666 cm.$^{-1}$; $\Delta\nu$ 1675 cm.$^{-1}$. This fact gives an evidence of the presence of a methyl group attached to the carbon atom of the double bond. The question whether the molecule of cedrene contains 1-methyl-cyclopentene-(1) ring or 1-methyl-cyclohexene-(1) ring is still unanswered from the study of the Raman effect.

Another possible evidence of the existence of the $-C=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-$ linkage in cedrene may be given by the occurrence of the Raman frequency of $\Delta\nu$ 1375 cm.$^{-1}$. This frequency has been observed in the Raman spectra of such molecules as methyl-butadiene, isoprene, chloropropylene, geraniol, linalool, pulegone, 1-methyl-cyclopentene-(1), 1-methyl-cyclohexene-(1), 1,2-dimethyl-cyclohexene, and 1-methyl-cycloheptene-(1), etc., but not in butadiene, cyclopentene, cyclohexene, and cycloheptene, etc., as shown in Table IX.

Summary.

The Raman spectrum of cedrene has been studied. The frequencies of $\Delta\nu$ 733, 780, 915 and 965 cm.$^{-1}$ are established to be attributable to the valency frequencies of the linkage, $-C-HC\overset{\displaystyle C}{\underset{\displaystyle C}{\diagdown\diagup}}$ or $-C-\overset{\displaystyle C}{\underset{\displaystyle C}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}-C-$ in the molecule of cedrene. The most intense line at $\Delta\nu$ 1666 cm.$^{-1}$ is assigned to characterize the C=C bond. The occurrence of the Raman line at $\Delta\nu$ 1375 cm.$^{-1}$ seems to give an evidence of the $-C=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-$ linkage in the cedrene molecule, $H_{20}C_{12}\overset{\displaystyle CH}{\underset{\displaystyle C-CH_3}{\diagup\!\!\parallel\!\!\diagdown}}$.

In conclusion, the authors wish to express their thanks to Ass. Prof. T. Nozoe for his kind advices and supply of the sample. The authors express their indebtedness also to Dr. Ichikawa for his supply of cedrol.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. III. THE ISOLATION AND CONSTITUTION OF MOROCTIC ACID $C_{18}H_{28}O_2$.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received March 25th, 1935. Published June 28th, 1935.

In the first paper(1) of this series it was shown concerning the highly unsaturated C_{18}-acids of sardine oil that the sardine oil contained an octadecatetraenoic acid $C_{18}H_{28}O_2$, and also the occurrence of an octadecatrienoic acid $C_{18}H_{30}O_2$ was indicated. In this paper the results of our further experiments concerning the octadecatetraenoic acid are described. Whilst this acid could not be isolated in the previous experiments, we have this time achieved its isolation by using a large quantity of sardine oil. Although the occurrence of octadecatetraenoic acid in sardine oil and in other marine animal oils has hitherto been stated by various authors, the acids described as an octadecatetraenoic acid by earlier authors represented, in some cases, a mixture of several highly unsaturated acids, and no octadecatetraenoic acid appears to have been isolated with certainty before our experiments. We designate the octadecatetraenoic acid isolated from sardine oil as moroctic acid.(2)

In order to determine the constitution of moroctic acid, methyl moroctate was oxidised by the ozonide method in the first place. Among the decomposition products of the ozonide, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde, acetic acid, acetaldehyde, carbon dioxide, methyl hydrogen succinate and the corresponding semi-aldehyde were recognised; the presence of malonic acid was also indicated. Of these decomposition products, propionic acid and propyl aldehyde are derived from the $CH_3{\cdot}CH_2{\cdot}CH=$ group, while succinic acid and its semi-aldehyde from the $=CH{\cdot}(CH_2)_2{\cdot}CH=$ group, and it was found from the yield of succinic acid and its semi-aldehyde that methyl moroctate contained two of the $=CH{\cdot}(CH_2)_2{\cdot}CH=$ group. The presence of acetic acid, acetaldehyde, carbon dioxide together with malonic acid is explainable

* Translated from the paper published in Japanese in the Report of Tokyo Imperial Industrial Research Laboratory, **27** (1932), No. 2.

(1) Toyama and Tsuchiya, this Bulletin, **4** (1929), 83.

(2) The name is derived from "Morokuti" (Japanese) which is one of a few other names given to Japanese sardine.

on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group which on oxidation yields primarily malonic acid and the corresponding aldehyde, from which acetic acid, acetaldehyde and carbon dioxide are formed by the secondary decompositions thus: $HOOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COOH + CO_2$ or $HOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COH + CO_2$. Finally the methyl hydrogen succinate and the corresponding semi-aldehyde are derived from the $=CH\cdot(CH_2)_2\cdot COOCH_3$ group, showing that free moroctic acid has the $=CH\cdot(CH_2)_2\cdot COOH$ group. From these results, moroctic acid is found to contain the following groups: $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot CH=$ (two), and $=CH\cdot(CH_2)_2\cdot COOH$. Accordingly its constitution is expressed by one of the following formulae:

$$CH_3\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (I)$$

$$CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (II)$$

$$CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (III)$$

In order to determine which of these formulae is correct, we have successfully applied the principle of selective addition of thiocyanogen to the poly-ethylenic acids.[3] After having found by determining the thiocyanogen value of methyl moroctate that thiocyanogen adds selectively to two of the four ethylenic linkings in methyl moroctate, yielding a tetrathiocyanate, we have prepared tetrathiocyanate of methyl moroctate and subjected the latter to ozonolysis. Among the decomposition products, propionic acid, propyl aldehyde, acetic acid, acetaldehyde, carbon dioxide and an oily substance containing thiocyano-groups were recognised; also malonic acid seemed to be present. Of these products, propionic acid and propyl aldehyde are derived from the $CH_3\cdot CH_2\cdot CH=$ group, and acetic acid, acetaldehyde and carbon dioxide together with malonic acid are considered to come from the $=CH\cdot CH_2\cdot CH=$ group. It is seen from these results that the two groups, $CH_3\cdot CH_2\cdot CH=$ and $=CH\cdot CH_2\cdot CH=$, in methyl moroctate remained unsaturated when thiocyanogen was allowed to act upon methyl moroctate. Of the three formulae given above, only the formula (I) is consistent with these facts, and it should be concluded that tetrathiocyanate of methyl moroctate is formed by the selective addition of thiocyanogen to the two ethylenic linkings (4:5 and 8:9) lying near the carboxyl group in the formula (I), leaving the other two ethylenic linkings (12:13 and 15:16) unsaturated. The oily substance formed on ozonolysis of tetrathiocyanate had still thiocyano-groups. It must, therefore, contain monomethyl ester of 3,4,7,8-tetrathiocyano-

(3) P. H. Kaufmann, *Arch. Pharm.*, **263** (1925), 675.

decane- 1,10-dicarboxylic acid. This was verified by the fact that on elimination of thiocyanogen from the oily substance followed by hydrolysis, there was obtained a decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid) which yielded on hydrogenation decane-dicarboxylic acid. From these results, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid expressed by the formula (I).

Of the unsaturated C_{18}-acids found in the natural fats and oils, the most widely distributed acids are oleic ($\Delta^{9:10}$), linolic ($\Delta^{9:10,\ 12:13}$), and linolenic ($\Delta^{9:10,\ 12:13,\ 15:16}$) acids. Comparing these acids with moroctic acid, there exist the following relations between the positions of respective ethylenic linkings. Thus the 9:10 ethylenic linking is common to oleic, linolic and linolenic acids, but it does not occur in moroctic acid; the 12:13 ethylenic linking is common to linolic, linolenic and moroctic acids, while the 15:16 ethylenic linking is common to linolenic and moroctic acids. Although there are found, besides the above-mentioned acids, petroselinic ($\Delta^{6:7}$), vaccenic ($\Delta^{11:12}$), γ-linolenic ($\Delta^{6:7,\ 9:10,\ 12:13}$),[4] and elaeostearic ($\Delta^{9:10,\ 11:12,\ 13:14}$) acids as naturally occurring unsaturated C_{18}-acids, neither 4:5 nor 8:9 ethylenic linking occurs in these acids except moroctic acid.

Experimental.

1. **The Isolation and Properties of Moroctic Acid and its Methyl Ester.** The ethyl esters (60 kg.) obtained by ethanolysis of sardine oil were subjected to distillation, and the distillate (28.5 kg.) boiling below 215°/10 mm. was collected separately. This was converted into free fatty acids, and the latter were dissolved in 85% methanol and cooled to separate crystalline solids which were filtered off. An aqueous solution of lithium hydroxide was added to the filtrate, and the insoluble lithium soaps were filtered. From the filtrate, the remaining fatty acids (7.5 kg.) were recovered and converted into methyl esters, from which a fraction (5.9 kg.) boiling below 215°/15 mm. was obtained on distillation. This was brominated in ethereal solution, and the ether insoluble bromides obtained were separated by means of benzene. The details of the above experiments were already described in the previous report[5] in which the benzene soluble bromides (1.5 kg.) were worked up for the isolation of hiragonic acid. In this paper the benzene insoluble bromides (900 g.) were debrominated and the product was fractionated to yield methyl moroctate. The debromination of the benzene insoluble bromides was carried out as follows: to the mixture of 100 g. of the bromides and 50 g. of zinc powder, 150 c.c. of alcohol was added. Unlike the case with the benzene soluble bromides described in the previous report, no appreciable heat evolution occurred. The mixture was gently refluxed by heating on the

(4) A. Eibner, L. Widenmayer and E. Schild, *Chemische Umschau Fette, Oele, Wachse und Harze*, **34** (1927), 312.

(5) This Bulletin, **10** (1935), 192.

water-bath, and 150 c.c. of 5 N alcoholic solution of hydrogen chloride was added in the course of 2.5 hours, another 50 g. of zinc powder being added in several portions. When all the alcoholic solution of hydrogen chloride has been added, heating was continued for one hour more, after which the alcoholic solution was removed by decantation. The residual insoluble substance was again refluxed with alcohol and zinc powder, and alcoholic solution of hydrogen chloride was added as before. The alcoholic solution was filtered, and the final residue was washed with alcohol. From the united alcoholic solution, the debrominated products were separated on addition of a large quantity of water, and extracted with ether. Since the products obtained from the ethereal solution were suspected to contain unsaponifiable substance, though it might have been a minute amount, they were saponified and the resulting soap solution was extracted with ether to remove unsaponifiable substance, after which the soap solution was decomposed with hydrochloric acid to yield the free fatty acids, and then the latter were reconverted into methyl esters. From 900 g. of the bromides there were obtained 220 g. of debrominated methyl esters. These were repeatedly fractionated, and a fraction (48 g.) boiling at 208–213°/15 mm. was finally obtained as methyl moroctate; d_4^{15} 0.9174, d_4^{20} 0.9140, n_D^{15} 1.4849, n_D^{20} 1.4829, mol. refr. 90.66 (calc. for $C_{19}H_{35}O_2\overline{F}$: 89.73), saponification value 193.3 (calc. 193.3), iodine value by the Rosenmund-Kuhnhenn method 344.6 (calc. 349.8), thiocyanogen value 173.1 (calc. for the formation of tetrathiocyanate $C_{19}H_{35}O_2(SCN)_4$: 174.9). On brominating methyl moroctate in ethereal solution, it yielded 57% of ether insoluble bromide which melted at about 215° to a tar-like substance (Found: Br, 68.65. Calc. for $C_{19}H_{37}O_2Br_6$: Br, 68.78%).

Moroctic acid liberated from its methyl ester in the usual way had the following constants (Found: C, 78.12; H, 10.25. Calc. for $C_{18}H_{28}O_2$: C, 78.20; H, 10.22%): d_4^{15} 0.9334, d_4^{20} 0.9297, n_D^{15} 1.4930, n_D^{20} 1.4911, mol. refr. 86.00 (calc. for $C_{18}H_{29}O_2\overline{F}$: 84.99),[6] neutralisation value 201.7 (calc. 203.1), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 372.6 and 361.9 respectively (calc. 367.6). On brominating moroctic acid in ethereal solution, it yielded 58% of ether insoluble bromide which melted at about 220° to a tar-like substance (Found: Br, 69.72. Calc. for $C_{18}H_{28}O_2Br_6$: Br, 69.83%). The hydrogenation product of moroctic acid yielded, after recrystallisation from 95% alcohol, a pure stearic acid; neutr. value 196.7 (calc. 197.4), m.p. and mixed m.p. 69.5–70°.

2. **Ozonolysis of Methyl Moroctate.** Methyl moroctate (5 g.) was dissolved in chloroform (50 c.c.), cooled with ice-salt, and a current of ozonised oxygen was passed through the solution until it became saturated, after which the chloroform was distilled by heating on the water-bath under diminished pressure. As it was found by a preliminary experiment that the ozonide was exceedingly unstable and decomposed explosively on undue heating, the temperature of water-bath was kept at about 40°C. When most of the chloroform was driven off, the distillation was stopped since there was a danger of frothing of the residue. The ozonide remained as a light yellow viscous liquid which is probably not a normal ozonide but an ozonide peroxide. From

(6) It should be noted here that moroctic acid and its methyl ester, like hiragonic acid, showed a slight exaltation of mol. refr. This was also observed with decadienedicarboxylic acid which was obtained in the experiments of the ozonolysis of tetrathiocyanate described below. The cause of this exaltation of mol. refr. is unknown to us.

20 g. of methyl moroctate, there was obtained 35 g. of ozonide (175%) which was not thoroughly freed from chloroform. The calculated yields for normal ozonide $C_{19}H_{36}O_{11}$ and ozonide peroxide $C_{19}H_{36}O_{12}$ are 165.9 and 171.4%, respectively. Water (200 c.c.) was then added to the ozonide in a flask, and the liquid was heated for about 30 minutes on the water-bath in a current of hydrogen. In order to recover the volatile decomposition products carried over with hydrogen, the flask was attached by a delivery tube to another three flasks which were connected in succession, the first (**a**) being filled with 200 c.c. of water and cooled with ice, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The products of ozonolysis were thus separated into two parts: (i) volatile decomposition products and (ii) decomposition products which were not carried over with hydrogen.

(i) *Volatile decomposition products.* These were collected in three flasks (**a**, **b** and **c**) as stated above. The aqueous solution in the flask (**a**) gave a pink colouration with Schiff's reagent and indicated the presence of acetaldehyde by a deep blue colouration produced on adding diethylamine and sodium nitroprusside. On adding phenylhydrazine, it yielded an oily phenylhydrazone which, after being washed with acetic acid, was heated with zinc chloride to 180°, when a smell of scatol was recognised, and consequently the presence of propyl aldehyde in the aqueous solution in the flask (**a**) was indicated. In order to effect a partial separation of acetaldehyde and propyl aldehyde, 50 c.c. of the aqueous solution was heated in a flask ($\mathbf{a}_1$) to 45°, and a current of carbon dioxide was passed through the solution to drive off the volatile portion at 45°; it was then caught by means of passing through an ice-cold water in another flask ($\mathbf{a}_2$) which was connected to the flask ($\mathbf{a}_1$) by a delivery tube. The solution remained in the flask ($\mathbf{a}_1$) precipitated, on adding *p*-nitrophenylhydrazine and hydrochloric acid, 0.7 g. of *p*-nitrophenylhydrazone which on recrystallisation from 50% alcohol yielded an impure *p*-nitrophenylhydrazone of propyl aldehyde in orange yellow needles; m.p. 121.5–122° (Found: N, 21.82. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask ($\mathbf{a}_2$) yielded 0.5 g. of *p*-nitrophenylhydrazone which, on fractional crystallisation from 50% alcohol, gave 1st crop with m.p. 116.5–117°, 2nd crop with m.p. 115.5–116° and 3rd crop with m.p. 113–113.5°. The 1st crop was found to consist of a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde by analysis (Found: N, 22.83. Calc. for $C_9H_{11}O_2N_3$: N, 21.76. Calc. for $C_8H_9O_2N_3$: N, 23.46%).

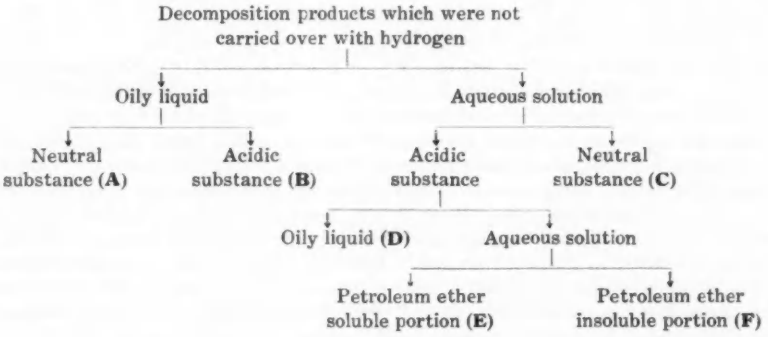
The solution in the flask (**a**) showed also acid reaction. On neutralising this solution (100 c.c.) with barium hydroxide and evaporating to dryness, there remained 0.25 g. of barium salt which was found to be barium acetate by analysis (Found: Ba, 53.30. Calc. for $C_4H_6O_4Ba$: Ba, 53.73%).

The barium hydroxide solution in the flask (**b**) was found to contain precipitate of barium carbonate, which was also formed in a smaller amount in the solution of the flask (**c**). The quantity of carbon dioxide formed by the ozonolysis is calculated from the quantity of the barium carbonate as 2.58 g. or 12.9% of the methyl moroctate used for ozonolysis. The formation of carbon dioxide in such a large amount is explainable on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group. The latter on ozonolysis yields malonic acid and its semi-aldehyde which, however, undergo secondary decompositions with the formation of carbon dioxide together with acetaldehyde and acetic acid, and the yield of carbon dioxide is 15.2% of methyl moroctate when the secondary decompositions take place to a quantitative extent. The reason

why the yield of carbon dioxide was not quantitative in this experiment may be attributed to the fact that a part of the primary decomposition products escaped the secondary decomposition and remained unchanged.

(ii) *Decomposition products which were not carried over with hydrogen.* A portion of these products separated under aqueous solution as an oily liquid. This was neutralised with sodium carbonate solution, the resulting solution was extracted with ether, and after distilling off the ether from ethereal solution, there remained a neutral substance (**A**). The neutralised solution, separated from ethereal extracts, was acidified with hydrochloric acid and an acidic substance (**B**) liberated was taken up with ether. The aqueous solution, separated from the oily liquid, was shaken with 2 l. of ether in order to extract the decomposition products thoroughly from the aqueous solution. The ethereal solution was concentrated to about 200 c.c., and then shaken with sodium carbonate solution to remove the acidic substance as sodium salts. The ethereal solution left behind a neutral substance (**C**) on distilling off ether. The carbonate solution containing the sodium salts of acidic substance was acidified, and the acidic substance liberated was taken up with ether. After distilling off the ether, 60 c.c. of water was added to the residue; a portion remained undissolved as an oily liquid (**D**) which was separated by filtration. The aqueous solution which contained dissolved substances was extracted with ether, and the product obtained on distilling off the ether was then treated with petroleum ether in order to effect a separation into petroleum ether soluble portion (**E**) and petroleum ether insoluble portion (**F**). The portions obtained by these separative operations are shown in Table 1.

Table 1.



Neutral substance (**A**). Yield 0.7 g. It had saponif. value 477.4 which is close to the saponif. value 483.4 for methyl ester of succinic semi-aldehyde $C_5H_8O_3$. After saponification it was subjected to oxidation with potassium permanganate in alkaline solution, and the crystalline product obtained on acidification showed, after being washed with a little ether, neutr. value 948.1 (calc. for succinic acid $C_4H_6O_4$: 950.6) and m.p. 180–180.5° which was not lowered when the substance was admixed with a pure specimen of succinic acid, m.p. 182.5–183°.

Acidic substance (**B** and **D** united). Yield 6.3 g., neutr. value 422.9, saponif. value 830.5 Although the neutr. value agrees with the calculated value for methyl hydrogen succinate $C_5H_8O_4$ (neutr. value 424.9; saponif. value 849.7), and the saponif. value is also close to the calculated value for methyl hydrogen succinate, the acidic substance obtained is an oily liquid at the ordinary temperature and it is considered to contain some other compounds besides methyl hydrogen succinate, since the melting point of the latter is recorded as 58° by Bone, Sudborough, and Sprankling.(7) The free acid obtained on saponification followed by acidification yielded, however, a pure succinic acid with neutr. value 948.5 and m.p. 182–183° after being recrystallised from ethyl acetate.

Neutral substance obtained from aqueous solution (**C**). Yield 1.2 g. It consisted of an orange yellow liquid and had saponif. value 380.4. After saponification, it was subjected to the permanganate oxidation in alkaline solution, and the crystalline product obtained on acidification showed neutr. value 940.9 and m.p. 178.5–179° after being washed with a little ether, and it was considered to be an impure succinic acid. Accordingly, this portion seems to contain methyl ester of succinic semi-aldehyde and in addition succinic aldehyde (or its polymerised products).

Petroleum ether soluble portion (**E**). On distilling off the petroleum ether from the solution, the distillate showed acid reaction. The barium salt prepared from the distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.01. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (2.7 g.) obtained on distilling off petroleum ether was a reddish orange liquid. On heating in an oil bath, about 1 g. of colourless distillate was obtained between 120–180° (temperature of bath). The distillate was neutralised with sodium hydroxide solution, and silver nitrate solution was added to precipitate silver salts fractionally; those were found to be a mixture of silver acetate and silver propionate by analyses (Found for 1st precipitate: Ag, 60.61. Found for 2nd precipitate: Ag, 62.45. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

Petroleum ether insoluble portion (**F**). Yield 15.4 g. This portion consisted of a reddish orange liquid and a crystalline solid. On oxidation with alkaline permanganate, there was obtained, after acidification, a white crystalline product which yielded succinic acid on recrystallisation from ethyl acetate; neutr. value 948.1, m.p. 182.5–183°. On concentrating the mother liquor, a further quantity of succinic acid separated, and after all the ethyl acetate being driven off, there remained a soft solid. A little water was added to the residue, a small portion of insoluble substance was removed, and the aqueous solution was shaken with ether in order to extract the substance dissolved in aqueous solution. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.8 g., neutr. value 1010, m.p. 124.5–125°), which decomposed on heating at 140–150° with the formation of carbon dioxide, and it was considered to contain malonic acid (neutr. value 1079, m.p. 133°). From these results, the petroleum ether insoluble portion is found to consist principally of succinic acid and its semi-aldehyde though a little malonic acid was contained in addition to these compounds. Whilst the maximum yield of succinic acid is 40.67% if methyl moroctate has only one $=CH\cdot(CH_2)_2\cdot CH=$ group, the yield of petroleum ether insoluble portion obtained in these experiments is 77% of the methyl moroctate

(7) *J. Chem. Soc.*, **85** (1904), 539.

used for ozonolysis. Accordingly, methyl moroctate must have two of the $=CH\cdot(CH_2)_2\cdot CH=$ group.

3. **Ozonolysis of Methyl Tetrathiocyano-moroctate.** Methyl moroctate (5 g.) was dissolved in 50 c.c. of glacial acetic acid, and 350 c.c. of 1/2 N thiocyanogen solution in glacial acetic acid was added. After being allowed to stand for 24 hours, the excess of thiocyanogen was removed by sodium thiosulphate solution. Methyl tetrathiocyano-moroctate was extracted with chloroform, and the chloroform solution was washed with water, dehydrated, and then concentrated to about 50 c.c. A current of ozonised oxygen was passed through the solution cooled with ice-salt until it became saturated. After distilling off chloroform from the solution, the ozonide remained as a reddish orange syrup. The last traces of chloroform could not be driven off owing to the frothing of the residual ozonide. Fifteen g. of methyl moroctate yielded 35 g. of ozonide (probably ozonide peroxide), from which the chloroform was not thoroughly removed. The calculated yield for ozonide peroxide $C_{19}H_{30}O_9(SCN)_4$ is 32.8 g. Water (150 c.c.) was added to the ozonide thus obtained, and the liquid was heated on the water-bath for 30 minutes. During heating, a current of hydrogen was passed through the flask containing the ozonide, and the volatile substance was carried over with hydrogen into another three flasks which were connected in succession, the first (**a**) being filled with 150 c.c. of water, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The decomposition products remained in the initial flask consisted of aqueous solution and insoluble oil which separated under aqueous layer. By these treatments, the decomposition products of ozonide were separated into three portions: (i) volatile substance, (ii) aqueous solution and (iii) oily substance.

(i) *Volatile substance.* The volatile substance collected in three flasks (**a**, **b** and **c**) was examined. In the aqueous solution of the flask (**a**), the presence of acetaldehyde was indicated by a deep blue colouration exhibited on adding diethylamine and sodium nitroprusside. Also the presence of propyl aldehyde was indicated by preparing phenylhydrazone and heating the latter with zinc chloride to 180°, when a smell of scatol was recognised. A partial separation of two aldehydes was attempted by passing carbon dioxide through the solution (50 c.c.) in a flask ($\mathbf{a}_1$) which was kept at 45°, and by collecting the volatilised portion, carried over with carbon dioxide, in another flask ($\mathbf{a}_2$) containing ice-cold water. The solution remained in the initial flask ($\mathbf{a}_1$) yielded 0.6 g. of crystalline *p*-nitrophenylhydrazone which melted at 121–121.5° after recrystallising from 50% alcohol and was considered to be an impure *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.94. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask ($\mathbf{a}_2$) yielded 0.5 g. of *p*-nitrophenylhydrazone which melted at 115.5–116° after recrystallising from 50% alcohol and was considered to be a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde (Found: N, 22.73. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask (**a**) contained also acetic acid which was identified by preparing the barium salt (Found: Ba, 53.51. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%).

The barium hydroxide solution in the flask (**b**) was found to contain a precipitate of barium carbonate which was also precipitated in the solution of the flask (**c**) in a smaller amount. The quantity of carbon dioxide formed by the ozonolysis is

calculated from the quantity of the precipitate of barium carbonate as 12.1% of the methyl moroctate used in these experiments.

(ii) *Aqueous solution.* The decomposition products dissolved in water were extracted with 2 l. of ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether in order to separate it into petroleum ether soluble portion and petroleum ether insoluble portion. The petroleum ether which was driven off from the solution had the odour of acetic acid. The barium salt prepared from the petroleum ether distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.42. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (1.8 g.) obtained after distilling off petroleum ether was heated in an oil bath, and there was obtained about 0.5 g. of a colourless liquid distilling below 136°. The silver salts fractionally precipitated from the distillate were found to be a mixture of the silver salts of acetic and propionic acids (Found for 1st precipitate: Ag, 60.48. Found for 2nd precipitate: Ag, 62.58. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

The petroleum ether insoluble portion consisted of a soft solid (0.8 g.). On adding a little water, a portion remained insoluble and was removed, and the aqueous solution was extracted with ether. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.3 g., neutr. value 1020, m.p. 125–126°), which decomposed at about 140° forming carbon dioxide and was considered to consist mainly of malonic acid.

(iii) *Oily substance.* Yield 21 g. For the elimination of thiocyano-groups, 30 c.c. of alcohol and 20 g. of zinc powder were added to the oily substance, the mixture gently refluxed, and 30 c.c. of 5 N alcoholic solution of hydrogen chloride gradually added. The product was extracted with ether, and after distilling off ether from ethereal solution, the residue was saponified and the resulting soap solution was shaken with ether in order to remove the unsaponifiable portion. On acidification of soap solution, a reddish orange oil was obtained. This was converted into methyl ester and the latter was fractionated, yielding a fraction boiling at 170–180°/10 mm., from which a free acid consisting of decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid) was liberated in the usual way (Found: C, 63.57; H, 8.13. Calc. for $C_{12}H_{18}O_4$: C, 63.68; H, 8.02%). It had d_4^{20} 0.9989, n_D^{20} 1.4535, mol. refr. 61.25 (calc. for $C_{12}H_{18}O_4$: 59.76), neutr. value 495.0 (calc. 496.2), iodine value by the Rosenmund-Kuhnhenn method 220.1 (calc. 224.5). On hydrogenation it yielded decane-1,10-dicarboxylic acid after recrystallising from 50% alcohol; neutr. value 484.8 (calc. for $C_{12}H_{22}O_4$: 487.5), m.p. 124.5–125°. Nördlinger[8] gives m.p. 124.5–125.5°; Chuit[9] gives m.p. 127.5–128°.

Summary.

Moroctic acid $C_{18}H_{28}O_2$ has been isolated from a large quantity of Japanese sardine oil. For the determination of its constitution, methyl moroctate was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde,

(8) *Ber.*, **23** (1890), 2356.
(9) *Helvetica Chim. Acta*, **9** (1926), 264.

methyl hydrogen succinate, methyl ester of succinic semi-aldehyde, carbon dioxide, acetic acid and acetaldehyde were found. Three last named compounds are considered to be formed by the secondary decomposition of malonic acid and the corresponding aldehyde which are derived from the $=CH\cdot CH_2\cdot CH=$ group. The presence of malonic acid, though in a small quantity, in the products of ozonolysis was also indicated. In the next place, tetrathiocyano-derivative was prepared from methyl moroctate, and it was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, carbon dioxide, acetic acid, acetaldehyde and an oily thiocyano-compound were recognised. The oily thiocyano-compound yielded, on elimination of thiocyanogen followed by hydrolysis, a decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid). Hence, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid which is expressed by the following formula.

$$CH_3\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH$$

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. IV. THE SEPARATION OF HIGHLY UNSATURATED C_{20}-ACIDS.

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Received March 25th, 1935. Published June 28th, 1935.

In previous reports[1] of this series, the highly unsaturated C_{16}- and C_{18}-acids of sardine oil were studied with the results that two individual components, hiragonic acid $C_{16}H_{26}O_2$ and moroctic acid $C_{18}H_{28}O_2$, were isolated and their constitutions were established as follows:

(1) This Bulletin, **4** (1929), 83; *ibid.*, **10** (1935), 192, 232.

Hiragonic acid : $CH_3{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_4{\cdot}COOH$

Moroctic acid: $CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}COOH$

The present paper deals with the highly unsaturated C_{20}-acids in sardine oil. The occurrence of highly unsaturated C_{20}-acids, such as $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, in sardine oil has already been reported by several authors, among whom Majima and Okada,[2] Tsujimoto,[3] and Brown and Beal[4] may be mentioned. Furthermore, such highly unsaturated C_{20}-acids have been found to occur also in various kinds of marine animal oils besides the sardine oil. Thus, we[5] found the acids $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$ in several kinds of whale oils (oils obtained from the whales belonging to *Mysticete*), in cod liver oil, in sperm body oil, in several kinds of liver oils from *Elasmobranch* fish, and also in pilot-whale head and body oils. Tsujimoto and his coworkers[6] reported the presence of highly unsaturated C_{20}-acids in giebel oil, herring roe oil, eel oil, the liver oil from *Chionecetes phalangium*, cod liver oil, the oil from *Atheresthes evermanni*, halibut liver oil, and in the liver oil from *Paralithodes camtschatica*. According to Ueno and Iwai,[7] menuke oil and the liver oil from *Scoliodon laticaudes* contain a highly unsaturated acid $C_{20}H_{32}O_2$. Suzuki and his coworkers,[8] examining the glycerides of marine animal oils, stated the occurrence of an acid $C_{20}H_{32}O_2$ as glycerides in whale oil, cod liver oil, herring oil, sardine oil, sand eel oil, cuttle-fish oil, red salmon oil, shark oil and in the liver oil from *Theragra chalcogramma*. A glyceride containing an acid component $C_{20}H_{30}O_2$ was stated by I. Okada[9] to occur in tunny oil, whereas an acid $C_{20}H_{32}O_2$ was considered by Tomiyama[10] to occur in tunny liver oil. Bull[11] stated the occurrence of the acids $C_{20}H_{30}O_2$ and $C_{20}H_{28}O_2$ in cod

(2) *J. Tokyo Chem. Soc.*, **35** (1914), 13.

(3) *J. Soc. Chem. Ind. Japan*, **26** (1923), 1013.

(4) *J. Am. Chem. Soc.*, **45** (1923), 1289.

(5) Toyama, *J. Soc. Chem. Ind. Japan*, **28** (1925), 95, 104; *ibid.*, **29** (1926), 531, 538, 624; *ibid.*, **30** (1927), 519; Toyama and Tsuchiya, *ibid.*, **30** (1927), 63, 116, 207; Toyama, *Report of the Tokyo Imperial Industrial Research Laboratory*, **27** (1932), No. 2.

(6) Tsujimoto, *Report of the Tokyo Imperial Industrial Research Laboratory*, **18** (1923), No. 2; Tsujimoto and Koyanagi, *ibid.*, **25** (1930), No. 4; Tsujimoto, *ibid.*, **26** (1931), No. 10; *ibid.*, **27** (1932), No. 15; Tsujimoto and Kimura, *J. Soc. Chem. Ind. Japan*, **26** (1923), 1162; Tsujimoto, *ibid.*, **30** (1927), 402; *ibid.*, **31** (1928), 136, 1191.

(7) *J. Soc. Chem. Ind. Japan*, **37** (1934), 121, 562.

(8) *Proc. Imp. Acad. Japan*, **5** (1929), 265, 269.

(9) *Journal of the Imperial Fisheries Institute*, **28** (1932), 105.

(10) *Bulletin of the Japanese Society of Scientific Fisheries*, **2** (1933), No. 1.

(11) *Tidskrift Kemi Farm. Terapi*, **14** (1917), 11.

liver oil. Brown and Beal[12] indicated the presence of two highly unsaturated C_{20}-acids, $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, in menhaden, cod liver, herring and salmon oils besides sardine oil. It is seen from the foregoing notes that the highly unsaturated C_{20}-acids, such as $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, occur widely in various kinds of marine animal oils, including sardine oil, but no individual acid has hitherto been isolated with certainty, and little has been known regarding the properties of these acids.

The above is a review of the most important works in literature on highly unsaturated C_{20}-acids in sardine and other marine animal oils. A survey of the literature shows that the highly unsaturated C_{20}-acids have also been found to occur in terrestrial animal oils. Thus Hartley[13] found an acid $C_{20}H_{32}O_2$ in the liver fats of pig and ox, which was termed afterward arachidonic acid by Lewkowitsch.[14] The presence of arachidonic acid in the fats from the organs of domestic animals has frequently been reported since then, but it appears not to have been isolated in a state of purity.

In the experiments described below, the highly unsaturated C_{20}-acids have been separated from sardine oil, and on a further separation into individual components, an eicosatetraenoic acid $C_{20}H_{32}O_2$ has been isolated in fairly pure state, and also a concentrated fraction of eicosapentenoic acid $C_{20}H_{30}O_2$ has been separated. Although the eicosatetraenoic acid in marine animal oils is described as arachidonic acid by some authors, it should not be assumed without experimental evidence that both acids are identical. In order to decide whether the eicosatetraenoic acid isolated from sardine oil, the constitution of which will be reported in a succeeding paper, is identical with arachidonic acid or not, it is necessary to gain a fuller information concerning arachidonic acid.

Experimental.

1. **Separation of Highly Unsaturated C_{20}-Acids.** As described in the second report,[15] 60 kg. of the ethyl esters, prepared by the ethanolysis of sardine oil, were subjected to distillation, and there was obtained 27 kg. of a fraction boiling over 215°/10 mm. Fifteen kg. of this fraction was used for this experiment. It was first

(12) *Loc. cit.*, (4).

(13) *J. Physiol.*, **38** (1909), 353.

(14) "Chemical Technology and Analysis of Oils, Fats and Waxes", 6th Edition, Vol. I, p. 215.

(15) This Bulletin, **10** (1935), 192.

treated by sodium-soap-acetone method,[16] and crude highly unsaturated acids having neutralisation value 179.3 and iodine value[17] 327.6 were obtained from the acetone-soluble sodium soaps. These were converted into methyl esters, and 8 kg. of the latter were subjected to fractional distillation with the results shown in Table 1.

During the distillation of the fraction (7), the temperature of bath was raised to about 260°, the pressure was reduced to 5 mm., and the distillation was continued till the rate of distillation became very slow. The large yield of the residue is probably caused by a partial polymerisation of methyl esters having high boiling point.

Table 1.

Fraction	B.p./10 mm.	Yield (g.)	n_D^{20}	Saponif. value	Iodine value
(1)	Below 210°	750	1.4700	189.0	245.7
(2)	210–215°	650	1.4766	181.4	275.8
(3)	215–220°	1020	1.4800	177.8	300.4
(4)	220–222°	900	1.4852	175.3	315.2
(5)	222–225°	850	1.4872	173.0	328.7
(6)	225–230°	600	1.4891	170.9	334.3
(7)	Over 230°	2050	1.4930	163.0	353.2
Residue and loss	—	1180	—	—	—

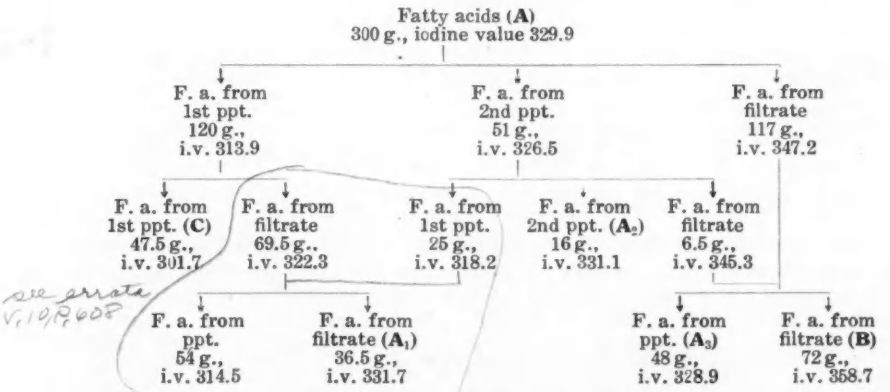
The fractions (3) and (4) were subjected to a further fractionation, and there was obtained a fraction boiling at 217–221°/10 mm.; saponif. value 177.0 and iodine value 303.0. Since this fraction was considered to contain a little of less unsaturated methyl esters, it was again treated by sodium-soap-acetone method, by which a small amount of acetone-insoluble sodium soaps was formed. The fatty acids liberated from acetone-soluble sodium soaps were then reconverted into methyl esters, and the latter were repeatedly fractionated to give 580 g. of a fraction boiling at 217–221°/10 mm.; saponif. value 177.0 and iodine value 316.0. The free fatty acids (**A**) obtained from this methyl ester fraction showed neutralisation value 185.0 and iodine value 329.9, and yielded 101% of ether insoluble bromides which had Br-content 69.41%. Hydrogenation yielded arachidic acid which had neutr. value 178.9 (calc. for $C_{20}H_{40}O_2$: 179.6) and m.p. 74–74.5° after recrystallisation from 95% alcohol. The melting point was not lowered when the substance was admixed with an authentic specimen of arachidic acid which was prepared from erucic acid by fusion with caustic potash and had m.p. 74.5–75°. Accordingly, the fatty acids (**A**) are proved to consist essentially of highly unsaturated C_{20}-acids. It is true that their iodine value is close to the calculated value (337.7) for the acid $C_{20}H_{32}O_2$, but they are found by the separative methods described below to contain other acids of different degrees of unsaturation in addition to the acid $C_{20}H_{32}O_2$.

(16) Toyama and Tsuchiya, *Chemische Umschau Fette, Oele, Wachse und Harze*, **32** (1925), 204; *ibid.*, **34** (1927), 51; also *J. Soc. Chem. Ind. Japan*, **28** (1925), 653, 962.

(17) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

2. **Fractional Precipitation of Sodium Soaps in Acetone.** The fatty acids (**A**) obtained above were fractionally precipitated from an acetone solution as their sodium soaps, and were separated into the portions of different degrees of unsaturation. The separative operation was carried out in the following manner: 50 g. of the fatty acids (A) were dissolved in 1 l. of acetone, and a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol was added to effect a partial neutralisation of the fatty acids, by which there was formed a precipitate of sodium soaps. After the precipitated sodium soaps were once brought into solution by a gentle boiling of the solution under a reflux condenser, the solution was allowed to cool to reprecipitate the sodium soaps which were then filtered. The filtrate was again neutralised partially by adding a portion of the sodium hydroxide solution, and after being treated as before, the precipitate of sodium soaps was filtered. Each precipitate of sodium soaps (1st and 2nd precipitates) was decomposed with hydrochloric acid to liberate the fatty acids. The remaining fatty acids in the filtrate were recovered by removing the solvent followed by acidification. The fatty acids (**A**) were thus separated into three portions, and each portion was subjected to a further separation by a similar operation as before. In these experiments, 300 g. of the fatty acids (**A**) were used instead of all the quantity of the fatty acids (**A**) obtained by the foregoing procedure. The results are given in Table 2.

Table 2.

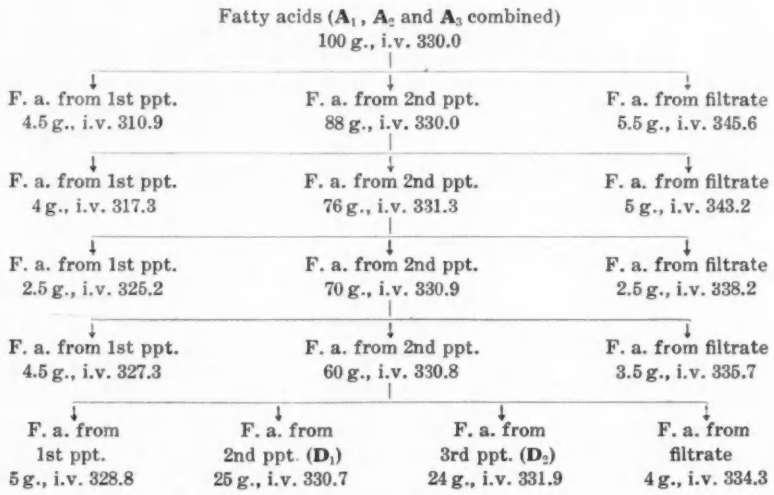

Fatty acids (A)
300 g., iodine value 329.9
F. a. from 1st ppt. 120 g., i.v. 313.9
F. a. from 2nd ppt. 51 g., i.v. 326.5
F. a. from filtrate 117 g., i.v. 347.2
F. a. from 1st ppt. (C) 47.5 g., i.v. 301.7
F. a. from filtrate 69.5 g., i.v. 322.3
F. a. from 1st ppt. 25 g., i.v. 318.2
F. a. from 2nd ppt. (A2) 16 g., i.v. 331.1
F. a. from filtrate 6.5 g., i.v. 345.3
F. a. from ppt. 54 g., i.v. 314.5
F. a. from filtrate (A1) 36.5 g., i.v. 331.7
F. a. from ppt. (A3) 48 g., i.v. 328.9
F. a. from filtrate (B) 72 g., i.v. 358.7

From their iodine values, the fatty acids fractions ($\mathbf{A_1}$), ($\mathbf{A_2}$) and ($\mathbf{A_3}$) are considered to consist essentially of an acid $C_{20}H_{32}O_2$; the fraction (**B**) contains a more highly unsaturated acid $C_{20}H_{30}O_2$ in addition to the acid $C_{20}H_{32}O_2$, while the fraction (**C**) contains less unsaturated acids besides the acid $C_{20}H_{32}O_2$.

3. **Isolation of Eicosatetraenoic Acid $C_{20}H_{32}O_2$.** In order to isolate the eicosatetraenoic acid $C_{20}H_{32}O_2$ from the fatty acids fractions ($\mathbf{A_1}$), ($\mathbf{A_2}$) and ($\mathbf{A_3}$), 100 g. of the combined fractions (iodine value 330.0) were dissolved in 2.5 l. of acetone, and a small portion of the sodium hydroxide solution prepared by dissolving 50 g.

of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol was added, by which a small amount of the precipitate (1st precipitate) of sodium soaps was formed. This was filtered, and the filtrate was then neutralised completely with the same solution of sodium hydroxide. The precipitated sodium soaps (2nd precipitate) were filtered, and the fatty acids liberated on acidification were again subjected to fractional precipitation of sodium soaps in acetone as before. These separative operations were repeated till the results shown in Table 3 were obtained. In the final fractionation, the fatty acids were separated into four portions.

Table 3.


Fatty acids (A_1, A_2 and A_3 combined)
100 g., i.v. 330.0
F. a. from 1st ppt.
4.5 g., i.v. 310.9
F. a. from 2nd ppt.
88 g., i.v. 330.0
F. a. from filtrate
5.5 g., i.v. 345.6
F. a. from 1st ppt.
4 g., i.v. 317.3
F. a. from 2nd ppt.
76 g., i.v. 331.3
F. a. from filtrate
5 g., i.v. 343.2
F. a. from 1st ppt.
2.5 g., i.v. 325.2
F. a. from 2nd ppt.
70 g., i.v. 330.9
F. a. from filtrate
2.5 g., i.v. 338.2
F. a. from 1st ppt.
4.5 g., i.v. 327.3
F. a. from 2nd ppt.
60 g., i.v. 330.8
F. a. from filtrate
3.5 g., i.v. 335.7
F. a. from 1st ppt.
5 g., i.v. 328.8
F. a. from 2nd ppt. (D_1)
25 g., i.v. 330.7
F. a. from 3rd ppt. (D_2)
24 g., i.v. 331.9
F. a. from filtrate
4 g., i.v. 334.3

The fatty acids fractions obtained by the final fractionation in Table 3 showed the iodine values which were close to each other. The fractions (D_1) and (D_2) were converted into methyl esters, and the latter were subjected to a repeated fractional distillation which yielded a fraction boiling at 217–220°/10 mm. as methyl eicosatetraenoate. It had the following constants: d_4^{15} 0.9140, d_4^{20} 0.9106, n_D^{15} 1.4854, n_D^{20} 1.4834, mol. refr. 99.87 (calc. for $C_{21}H_{34}O_2$: 98.96), saponif. value 176.0 (calc. 176.3), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 321.2 and 309.5 respectively (calc. 319.0), thiocyanogen value 160.5 (calc. for the formation of tetrathiocyanate: 159.5). Bromination in ethereal solution yielded 103% of ether insoluble bromide (Found: Br, 67.02. Calc. for $C_{21}H_{34}O_2Br_8$: Br, 66.76%).

The eicosatetraenoic acid liberated from the methyl ester in the usual way showed the following constants: d_4^{15} 0.9300, d_4^{20} 0.9263, n_D^{15} 1.4935, n_D^{20} 1.4915, mol. refr. 95.16 (calc. for $C_{20}H_{32}O_2$: 94.23), neutralisation value 184.3 (calc. 184.4), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 334.0 and 323.1 respectively (calc. 333.7), thiocyanogen value 167.1 (calc. for the formation of tetrathiocyanate: 166.9). Bromination in ethereal solution yielded 103% of ether insoluble

bromide which turned black at about 240° without melting (Found: Br, 68.06. Calc. for $C_{20}H_{32}O_2$: Br, 67.76%).

4. **Separation of a Concentrated Fraction of Eicosapentenoic Acid $C_{20}H_{30}O_2$.** Seventy g. of the fatty acid fraction (**B**) recorded in Table 2 was dissolved in 1.8 l. of acetone, and a small quantity of the same solution of sodium hydroxide as used in the preceding separative operation was added in order to precipitate the less unsaturated fatty acids as their sodium soaps, which were filtered. The more highly unsaturated fatty acids recovered from the filtrate were again treated with the sodium hydroxide solution as before, the less unsaturated portion was removed as insoluble sodium soaps, and after several repetitions of these separative operations, there was obtained 8 g. of a fatty acid fraction from the final filtrate which had the following constants: d_4^{15} 0.9399, n_D^{15} 1.5019, neutr. value 185.1, iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 392.7 and 378.4 respectively, thiocyanogen value 167.9 (calc. for $C_{20}H_{30}O_2$: neutr. value 185.6, iodine value 419.9, thiocyanogen value calc. for the formation of tetrathiocyanate 168.0). Bromination in ethereal solution yielded 104% of ether insoluble bromide which turned black at about 240° without melting (Found: Br, 71.28. Calc. for $C_{20}H_{30}O_2Br_{10}$: Br, 72.56%). As the iodine value of this fraction is still considerably lower than the value calculated for $C_{20}H_{30}O_2$, it must contain an appreciable amount of $C_{20}H_{32}O_2$ in addition to $C_{20}H_{30}O_2$. Although the acid $C_{20}H_{30}O_2$ could not be isolated in pure state, its existence in sardine oil is thus proved by the present experiments.

5. **Examination of the Less Unsaturated Portion.** Forty-seven g. of the fatty acid fraction (**C**) recorded in Table 2 was dissolved in 1 l. of acetone and was partially neutralised by adding a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. The solution was refluxed until all the insoluble sodium soaps formed once disappeared, and then it was allowed to cool to reprecipitate the insoluble sodium soaps. By these treatments, the following two portions were separated.

	Yield (g.)	Neutr. value	Iodine value
(i) Fatty acids from insoluble sodium soaps	17	186.0	276.6
(ii) Fatty acids from the filtrate	29	185.0	315.9

The iodine value of the fatty acids (i) was more close to the calculated value for $C_{20}H_{34}O_2$ (248.6) than that for $C_{20}H_{32}O_2$ (333.7), but they yielded 71% of an ether insoluble bromide having Br-content 67.06% which was considerably higher than the Br-content of $C_{20}H_{34}O_2Br_6$ (61.02%) and was close to the Br-content of $C_{20}H_{32}O_2Br_8$ (67.76%). On the other hand, when the lithium soaps prepared from the fatty acids (i) were treated with 50% alcohol, there was obtained a small amount of the lithium soaps insoluble in 50% alcohol, and the latter yielded on acidification fatty acids with an iodine value 91.3 which indicated that the fatty acids (i) contained also a small amount of less unsaturated fatty acids such as $C_{20}H_{36}O_2$ (iodine value 81.8). Accordingly, the fatty acids (i) were found to be a mixture of the fatty acids of different degrees of unsaturation, and though the presence of $C_{20}H_{34}O_2$ was not proved with certainty, it was most probable.

Summary.

Highly unsaturated C_{20}-acids have been separated from sardine oil and they were further separated into the portions of different degrees of unsaturation with the results that an eicosatetraenoic acid $C_{20}H_{32}O_2$ was isolated and also the presence of an eicosapentenoic acid $C_{20}H_{30}O_2$ was proved by separating a fraction, in which this acid is concentrated.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. XI.

By **Tetsuya ISHIKAWA.**

Received March 25th, 1935. Published June 28th, 1935.

The nature of the solutional viscosity of solids in liquids. In the latest publication,[1] we have laid stress on the solutional viscosity in accordance with the Ishikawa's theory for elucidating the viscosity of aqueous solutions of electrolytes, and evaluated those values of a few strong electrolytes.

Table 1.

Substance	Solutional viscosity at t°C.	t°C.
Naphthalene	0.02653	25
Diphenyl	0.05413	25
KCl	0.01003	18
	0.00874	25
KI	0.00735	18
	0.00664	25
$RbNO_3$	0.00889	18
	0.00789	25
$CsNO_3$	0.00842	18
	0.00753	25

Since his formula for binary mixtures, the component viscosities of which being alike treated, has the validity for the solution of solids in liquids, one may arrive at the supposition that the solutional viscosity of a solid calculated by it touches a fundamental nature of the molecular constitution, and must have, in con-

(1) T. Ishikawa and T. Baba, this Bulletin, **10** (1935), 153.

sequence, an intimate relationship with the viscosity of its molten state.

The equations expressing the viscosity variation of liquids with temperature have been proposed numerously. Among them the one proposed by Raman[2] and developed by Andrade[3] and his follower[4] is simple but sufficient within the limit of experimental error:

$$\log \eta = \alpha + \frac{\beta}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

in which η denotes the viscosity, T the absolute temperature, α and β constants. The equation also proved to be valid for molten salts such as $NaNO_3$, KNO_3, and $PbBr_2$, but failed for some salts such as $PbCl_2$, for which, however, a slightly modified formula which was also proposed by Andrade was shown to be applicable:

$$\log \eta = \alpha + \frac{\beta}{T-\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where θ is a constant.

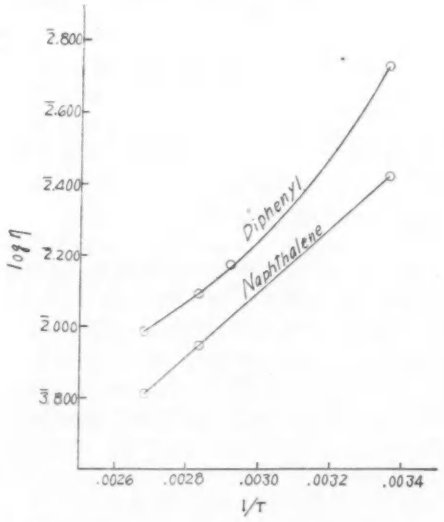

Table 2.

Naphthalene. Melting point: 80.1°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.02653	$\bar{2}.4237$	0.00336	0.02656
80	0.00886	$\bar{3}.9474$	0.00283	0.00886
100	0.00649	$\bar{3}.8125$	0.00268	0.00649

$$\log \eta_T = -4.1986 + 899.7\frac{1}{T}$$

Table 3.

Diphenyl. Melting point: 70.5°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.05413	$\bar{2}.7334$	0.00336	0.05413
70	0.01488	$\bar{2}.1727$	0.00292	0.01454
80	0.01243	$\bar{2}.0944$	0.00283	0.01243
100	0.00971	$\bar{3}.9872$	0.00268	0.00971

$$\log \eta_T = -2.6512 + \frac{88.85}{T-233.84}$$

(2) C. V. Raman, *Nature*, **111** (1923), 532.
(3) E. N. Da C. Andrade, *Nature*, **125** (1930), 309.
(4) B. Prasad, *Phil. Mag.*, **16** (1933), 263.

Fortunately the viscosity measurements of molten naphthalene at different temperatures were done by Kurnakow[5] and by Scheuer,[6] from their data the values at regular intervals of temperature being recalculated by Bingham and Spooner,[7] and those of diphenyl by these authors.[7] Taking logarithms of the viscosities against $1/T$ of each substance, we find that in the former case the points with our value at 25°C. strictly lie on a straight line, and in the latter case on a curve on which our value at 25°C. also lies as seen from the figure. Tables 2 and 3 show how the calculated values by the formulae and the observed compare numerically.

As to the viscosity of molten inorganic salts, there have been known, except the salts above cited, the measurements by Lorenz[8] on KCl, KBr, NaCl, and NaBr. Among them KCl only is available for the present purpose. So that, in the following we will consider the solutional viscosity of KCl. For the viscosity of the molten KCl, formula (1) is valid:

$$\log \eta_T = -3.4530 + 1705 \frac{1}{T},$$

and the calculated values are in good agreement with the observed as readily seen from Table 4.

Table 4.

Potassium chloride. Melting point: 768°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
790	0.0142	$\bar{2}.1523$	0.000941	0.0142
835	0.0121	$\bar{2}.0828$	0.000907	0.0124
920	0.0099	$\bar{3}.9956$	0.000838	0.0095
1035	0.0071	$\bar{3}.8513$	0.000765	0.0071

By the use of the equation, the extrapolated values at 25° and 18°C. are estimated thus:

$$\eta_{25} = 1.89 \times 10^2 \quad \text{and} \quad \eta_{18} = 2.55 \times 10^2,$$

respectively. These show too much higher values than would be expected from the consideration just made on organic non-electrolytes. And if we take the ratios at respective temperatures, they are respectively

$$\text{ratio at } 25° = 2.16 \times 10^4 \quad \text{and} \quad \text{ratio at } 18° = 2.53 \times 10^4.$$

The recent conception on the physics of solids[9] shall be introduced here.

(5) N. S. Kurnakow, *Z anorg. allg. Chem.*, **135** (1924), 84, 89.
(6) O. Scheuer, *Z. physik. Chem.*, **72** (1910), 553.
(7) E. C. Bingham and L. W. Spooner, *Physics*, **4** (1933), 393, 394.
(8) R. Lorenz, *Z. physik. Chem.*, **79** (1912), 65.
(9) "Handbuch der Physik", XXIV (Berlin, 1933), 803; F. Zwicky, *Rev. Mod. Physics*, **6** (1934), 193; A. Goetz, *Phys. Rev.*, **45** (1934), 138.

The existence of a crystalline state attributes mainly to the co-operative actions between many elementary particles such as atoms, ions, etc. These interactions extend over distances which are enormously greater than usual action radii of elementary particles, and the co-operative actions, in general, necessitate the introduction of a secondary structure of crystals, or without such conception real crystals which display structure sensitive properties such as the elastic limit, the breaking strength, the thermal and the electrical conductivity, etc. cannot satisfactorily be described by the theory of ideal lattices. By this theory the energetic aspects of the ideal states are already roughly realized in a statistical manner in the melt. It follows that the heat of fusion of the crystal is roughly the same as the gain in energy by a variation leading from the ideal state to the secondary structure, and that an aggregation of groups of approximately equal size which is essential for the formation of a solid crystal takes place during an interval of temperature of a few degrees above the melting point, and that if their formation is prevented, undercooling results down to a temperature at which the group formation is more probable. As regards the dimension of the secondary structure, the theory tells us that a secondary structure superposes on top of the ordinary primary structure, showing perfect regularity also, or in other words the surface density of the plane of it is the same as the planes of free ionic lattices, and its dimension is for most of the crystals found in the region between 100 and 10000 Å, e.g. the plane of a secondary structure of NaCl is divided into 35 primary lattice spacings of cubic block of equal size or in a block of a secondary structure there are 2×10^4 ionic pairs in round number.

Now, the extrapolation of the Raman-Andrade formula far below the melting point as above treated simply means a supposed continuation of the molten state as in like manner as above the melting point, indifferent to the actual phenomenon whether or not the formation of the secondary structure occurs. But, so far as the formula is valid at or about the melting point, its employment far below the melting point should be based on the assumption that although the secondary structure already forms yet the solidification does not appear even at that temperature. This assumption is allowable also from the viscosity theory of simple liquids recently developed by Andrade,[10] who assumes that when a solid is melted it still retains in the liquid form sufficient of its crystalline character for the atoms or the molecules to possess a frequency of atomic or molecular vibration which is practically the same as that of the solid

(10) E. N. Da C. Andrade, *Nature*, **128** (1931), 835; *Phil. Mag.*, **17** (1934), 497.

form at the melting point, and derives a theoretical equation $\eta = \frac{4}{3}\frac{m\nu}{\sigma}$, m being the mass of an atom or a molecule, σ the average distance between the centers of atoms or molecules, and ν the frequency of vibration nearly concordant with the Lindemann formula.[11] Thus, for KCl ν(obs.) $= 4.74 \times 10^{12}$, $m = \frac{74.56}{6.06 \times 10^{23}}$, $\sigma = \left(\frac{74.56}{1.97 \times 6.06 \times 10^{23}}\right)^{1/3}$ and, therefore, the calculated viscosity at the melting point $\eta = 0.0196$, which gives a fair agreement with the extrapolated value 0.0153 from the exponential formula now in question.

From the above considerations together with the fact that the crystal structure of KCl is quite similar to that of NaCl, the ratios above obtained 2.16×10^4 and 2.53×10^4 at 25° and 18°C. respectively may undoubtedly correspond to the number of ionic pairs in a block of the secondary structure, taking for granted that the solutional viscosity of this salt is the viscosity due to its ionic pair.

Hence the following conclusion may be drawn: The solutional viscosity derived from the Ishikawa formula is the viscosity due to the block of a secondary structure in accordance with the secondary structure theory on crystals when the substance is an organic non-electrolyte, or is the viscosity due to the ionic pair when the substance is an ionic salt.

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ÜBER (+)- UND (−)-BIS-1,1′-β-TETRAHYDRO-DESOXY-CODEIN.[1]

Von **Kakuji GOTO** und **Hideo SHISHIDO.**

Eingegangen am 2. April, 1935. Ausgegeben am 28. Juni, 1935.

In der XXXIX. Mitteilung[2] haben wir berichtet, dass (+)- bzw. (−)-Dihydro-thebainon mittels $AgNO_3$ ins (+)- bzw. (−)-Bis-1,1′-dihydro-thebainon verknüpft werden kann. Nun wurde dieser Versuch auf

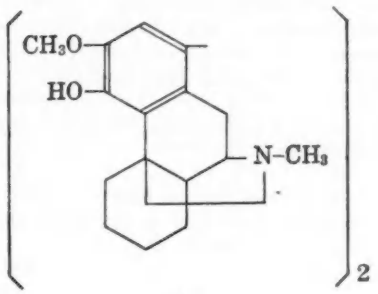
(11) F. A. Lindemann, *Physik. Z.*, **11** (1910), 609.
(1) XLI. Mitteilung über Sinomenin.
(2) *Ann.*, **511** (1934), 207.

Demethoxy-desoxo-dihydro-sinomenin ((+)-β-Tetrahydro-desoxy-codein) und (−)-β-Tetrahydro-desoxy-codein ausgedehnt und die entstandenen bimolekularen Basen wurden wohl racemisiert.

Betreffs des Hofmannschen Abbaues dieser Bis-1,1′-Base, gewinnt man bisher nur die Des-N-methyl-base und die N-freie Substanz, deren Analyse nicht genau mit der berechneten Wert übereinstimmt. So haben wir zurzeit verzichtet diesen Abbau weiter zu verfolgen.

Über den Hofmannschen Abbau von dem monomolekularen Demethoxy-desoxo-dihydrosinomenin haben wir schon früher berichtet.[3] Derselbe Abbau von β-Tetrahydro-desoxy-codein wurde hierbei unternommen und die betreffenden Zwischenprodukten aus Sinomenin und Thebain wurden racemisiert.

Das racemische Thebenan, aber, leider krystallisiert nicht in der gewöhnlichen Bedingungen des Laboratoriums.



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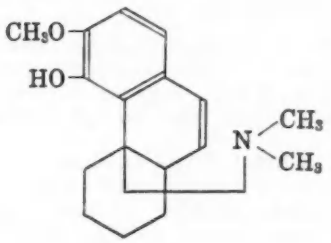

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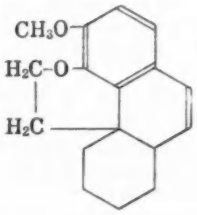

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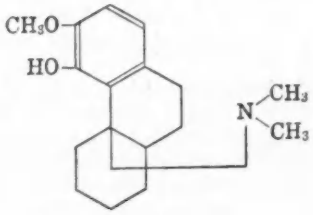

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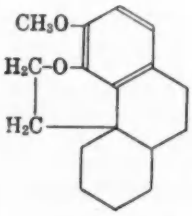

V

Versuche.

Bis-1, 1′-demethoxy-desoxo-dihydrosinomenin (I). Demethoxy-desoxo-dihydro-sinomenin (1 g.) wurde in 10 c.c. Methanol gelöst und in 50 c.c. Wasser unter

Umrührung eingegossen. Zu dieser Aufschwemmung wurde 0.5 g. $AgNO_3$, gelöst in 50 c.c. Wasser, zugegeben. Nach halber Stunde wurde das Reaktionsgemisch mit NaCl von Silberion befreit. Das Filtrat wurde mit Na_2CO_3 stark alkalisiert und mit Chloroform geschüttelt. Der Chloroform-Rückstand ergab, beim Umkrystallisieren aus Benzol, feine Prismen, welche nach nochmaliger Umkrystallisation bei 230–237° schmolzen. Ausbeute 0.6 g. Es zeigt die Diazo-reaktion nur bis auf 10^4-fache Verdünnung. (Gef.: C, 75.64; H, 8.22; N, 4.87; M. Gew. (Kampfer), 559; Ber. für $C_{36}H_{48}O_4N_2$ (572): C, 75.52; H, 8.39; N, 4.90%; M. Gew., 572. Spez. Drehung (0.1365 g. Subst. in 10 c.c. Äthanol): $[\alpha]_D^{20°} = +91.57°$.)

Jodmethylat. Bereitet durch Vereinigen beider Komponenten in Methanol. Aus Wasser umkrystallisiert, stellt es schöne, oktaedrische Prismen. Schmp. 275–279° (u. Zers.). (Gef.: I, 29.65. Ber. für $C_{38}H_{54}O_4N_2I_2$(856): I, 29.67%.)

Chlorhydrat. Krystallisiert aus 10-proz. Salzsäure. Auch umkrystallisierbar aus Wasser. Schmp. 293–297° (u. Zers.) (Gef.: Cl, 10.72. Ber. für $C_{36}H_{48}N_2O_4 \cdot 2HCl$: Cl, 11.01%.)

Bis-1, 1′-β-tetrahydro-desoxy-codein (I). Darstellung wie bei der (+)-Substanz. Ausbeute 0.2 g. aus 0.55 g. monomolekularer Substanz. Lange Prismen aus Benzol. Schmp. 230–238°. Diazoreaktion ebenso schwach wie bei (+)-Substanz. (Gef.: C, 75.40; H, 8.23; N, 4.79; M. Gew. (Kampfer), 569. Ber. für $C_{36}H_{48}O_4N_2$(572): C, 75.52; H, 8.39; N, 4.90%; M. Gew. 572. Spez. Drehung (0.0876 g. Subst. in 10 c.c. Äthanol): $[\alpha]_D^{20°} = -91.32°$. *Jodmethylat.* Dargestellt wie bei (+)-Substanz. Schmp. 276–279°. (Gef.: I, 29.50. Ber. für $C_{38}H_{54}O_4N_2I_2$(856): I, 29.67%.)

***d, l*-Bis-1, 1′-β-tetrahydro-desoxy-codein.** Je 50 mg. (+)- und (−)-Substanz wurden in Benzollösung vereinigt. Beim Verdünsten des Benzols krystallisierte die racemische Substanz in langen Prismen. Ausbeute 60 mg. Schmp. 255–260°. Kein Drehungsvermögen (0.0545 g. Subst. in 10 c.c. Äthanol und in 1 dm. Rohr, $\alpha = 0$).

Des-N-methyl-β-tetrahydro-desoxy-codein (II). Bereitet wie bei Des-N-methyl-demethoxy-desoxo-dihydro-sinomenin[3]. Schmp. 145–148°. Diazoreaktion positiv noch bei 2,000,000-facher Verdünnung. Rote Halochromie in konz. Schwefelsäure. (Gef.: C, 75.77; H, 9.06; N, 4.56. Ber. für $C_{19}H_{27}O_2N$ (301): C, 75.75; H, 8.97; N, 4.65%. Spez. Drehung (0.1314 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{22.5°} = +65.45°$).

***d, l*-Des-N-methyl-β-tetrahydro-desoxy-codein.** Je 0.2 g. (+)- und (−)-Des-N-methyl-β-tetrahydro-desoxy-codein wurden gesondert in Äther gelöst und vereinigt. Wurde der Äther verdampft, krystallisierte sich die racemische Substanz (0.25 g.) in schönen Prismen aus. Schmp. 133–136°. Die Substanz drehte die Polarisationsebene nicht (0.1827 g. Subst. in 10 c.c. Methanol und in 1 dm. Rohr, $\alpha = 0$).

(+)-Dehydro-thebenan (III) aus Codein. Darstellung wie bei (−)-Substanz aus Sinomenin.[3] Prismen. Schmp. 107–112°. Halochromie in konz. Schwefelsäure rot. (Gef.: C, 79.52; H, 8.04. Ber. für $C_{17}H_{20}O_2$(256): C, 79.69; H, 7.81%. Spez. Drehung (0.1766 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{27.5°} = +175.54$).

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(3) Dieses Bulletin, **6** (1931), 38, 205. Vgl. Small und Cohen, *J. Am. Chem. Soc.*, **54** (1932), 808.

***d, l*-Dehydro-thebenan.** Je 0.2 g. (+)- und (−)-Dehydro-thebenan wurde in Ätherlösung vereinigt. Daraus krystallisierte die racemische Substanz (0.22 g.) in Prismen aus. Schmp. 90–92°. $\alpha = 0$ (0.1810 g. Subst. in 10 c.c. Methanol und in 1 dm. Rohr).

Dihydro-des-N-methyl-β-tetrahydro-desoxy-codein (IV). Bedingung der katalytischen Reduktion wie bei der Darstellung von Dihydro-des-N-methyl-demethoxy-desoxo-dihydro-sinomenin.[3] Schmp. 161°. Diazo-reaktion bemerklich in 2,000,000-facher Verdünnung. Keine Halochromie in konz. Schwefelsäure. (Gef.: C, 75.32; H, 9.91; N, 4.52. Ber. für $C_{19}H_{29}O_2N$ (303): C, 75.25; H, 9.57; N, 4.61%. Spez. Drehung (0.1339 g. Subst. in 10 c.c. Methanol-Chloroform):[4] $[\alpha]_D^{22.5°} = -78.42°$).

***d, l*-Dihydro-des-N-methyl-β-tetrahydro-desoxy-codein.** Je 0.2 g. (−)- und (+)-Substanz wurde in Äther-methanollösung racemisiert. Ausbeute 0.24 g. Prismen, gesammelt in Rosetten. Schmp. 135–140°. $\alpha = 0$ (0.1775 g. Subst. in 10 c.c. Methanol-Chloroform und in 1 dm. Rohr).

(+)-Thebenan aus Codein (V). Dargestellt wie bei (−)-Thebenan[5] aus Sinomenin. Schmp. 48–54°. Zeigt keine Halochromie in konz. Schwefelsäure. (Gef.: C, 78.93; H, 8.82. Ber. für $C_{17}H_{22}O_2$ (258): C, 79.07; H, 8.53%. Spez. Drehung (0.2156 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{22.5°} = +3.25°$).

d, l-Thebenan konnte nicht bisher in Krystallen erhalten worden.

Chemisches Laboratorium, Kitasato-Institut,
Shiba, Tokyo.

ACETON-*d*-WEINSÄUREDIÄTHYLESTER UND SEINE OPTISCHE AKTIVITÄT.

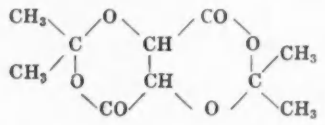
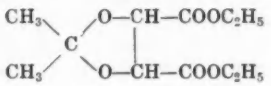
Von Yojiro TSUZUKI.

Eingegangen am 6. Juni, 1935. Ausgegeben am 28. Juni, 1935.

Über die Acetonverbindung der *d*-Weinsäure ist bisher nur eine Diacetonverbindung (I) bekannt,[1] und die Verbindung, welche den gleichen Acetonrest an den beiden alkoholischen Hydroxylen trägt, ist noch nicht erhalten. In der Absicht eine solche Verbindung zu gewinnen, habe ich versucht, *d*-Weinsäureester zu acetonieren. Fischer und Appel[2]

(4) Small u. Cohen geben einen niedrigeren Wert an (*loc. cit.*).
(5) (−)-Thebenan aus Sinomenin schmilzt auch bei 48–54°.
(1) H. O. L. Fischer und C. Traube, *Ber.*, **60** (1927), 485.
(2) H. O. L. Fischer und H. Appel, *Helvetica Chim. Acta*, **17** (1934), 1574.

haben vor einiger Zeit ausgesprochen, dass ihnen die Acetonierung von Weinsäuredimethylester bisher nach keiner der bekannten Methoden gelungen war; ich konnte aber ziemlich leicht die erzielte Acetonverbindung (II) synthetisieren, indem ich als Kondensationsmittel wasserfreies Kupfersulfat benutzte.

I  II 

Diese Verbindung ist, wie erwartet, stark linksdrehend.[3] Die spezifische Drehung ist konzentrations-unabhängig und die Rotationsdispersion ist einfach.[4] Über diese optische Versuche soll später ausführlich mitgeteilt werden.

Zur Darstellung wurden 30 g. Weinsäurediäthylester mit 50 g. wasserfreiem Kupfersulfat und 200 g. Aceton auf dem Wasserbad 36 Stunden gekocht. Nach Abfiltrieren von Kupfersulfat und Abdestillieren von Aceton wurde der dickflüssige Rückstand in Äther aufgenommen, und zur Entfernung unverändertes Esters mit gesättigter Borax-lösung zweimal geschüttelt. Die Ätherlösung wurde mit Natriumsulfat getrocknet, Äther verdampft, und der Rückstand in Vakuum destilliert. Farblose dicke Flüssigkeit. Ausbeute an reiner Substanz 20 g. Leicht löslich in meisten organischen Lösungsmitteln, unlöslich in Wasser. Siedep. 150° (korr., 19 mm.), d_4^{15} 1.1213, n_D^{20} 1.4334, $[\alpha]_D^{15}$ −51.19°. Gefunden: C, 53.17; H, 7.38; Aceton (nach Ripper),[5] 23.43. Berechnet für $C_{11}H_{18}O_6$ (246.14): C, 53.63; H, 7.37; Aceton, 23.58%.

Musashi Hochschule,
Tokio-Nakaarai.

(3) Analog gebaute Brückenderivate der *d*-Weinsäure sind alle stark linksdrehbar, wie z.B. Methylen-Weinsäure (Austin und Carpenter, *J. Chem. Soc.*, **125** (1924), 1943), Benzal-Weinsäuredimethylester (Fischer und Appel, *loc. cit.*).

(4) Über die Beziehung zwischen Konstitution und optischer Aktivität der Weinsäure und ihrer Derivate siehe z.B. T. M. Lowry, *Nature*, **117** (1926), 271, Austin und Carpenter, *loc. cit.*

(5) *Monatsh.* **21** (1900), 740, Vgl. H. Meyer, "Nachweis und Bestimmung org. Verbindungen", (1933), S. 60.

ERZEUGUNG DES LEICHTEN WASSERS UND DIE BESTIMMUNG DER DEUTERIUM-KONZENTRATION IM NORMALEN WASSER.

(Vorläufige Mitteilung.)

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Eine der zuverlässigen Methoden, die uns die Konzentration des Deuteriums im normalen Wasser bestimmen lassen, besteht darin, dass man das Wasser auf irgendeine Weise vom Deuterium befreit, und das spezifische Gewicht des so erzeugten leichten Wassers im Verhältnis zu dem normalen Wasser bestimmt. Nach dieser Richtung sind schon einige Versuche ausgeführt worden.[1] Die vorliegende Arbeit betrifft die Erzeugung des leichten Wassers aus Osaka Leitungswasser durch die fraktionierte Elektrolyse und die Bestimmung der Deuterium-Konzentration in demselben.

Das Leitungswasser wurde mit NaOH 0.5N gemacht und zwischen Nickel-Elektroden elektrolysiert. Der Knallgasstrom aus dem Elektrolysiergefäss wurde sorgfältig getrocknet und ebensogut getrocknete Luft zugesetzt. Das gemischte Gas wurde dann über das bis auf 300°C. erhitzte Kupferoxyd geleitet und katalytisch zu Wasser rekombiniert. Auf der ersten Stufe der Elektrolyse wurde nur 1/10 Volumen des originalen Wassers zersetzt und rekombiniert. Dem rekombinierten Wasser wurde wieder NaOH zugesetzt und dann wurde es der zweiten Stufe der Elektrolyse unterworfen. Aber auf dieser Stufe wurde 1/2 Volumen des Elektrolysierwassers zersetzt und rekombiniert. Das rekombinierte Wasser wurde für die dritte Stufe der Elektrolyse reserviert. Die dritte und die darauf folgenden Elektrolysen wurden auf ähnliche Weise wie die zweite Stufe durchgeführt. Nach jeder Stufe der Elektrolyse wurde das rekombinierte Wasser sorgfältig gereinigt und dessen spezifisches Gewicht im Verhältnis zu dem ebensogut gereinigten Osaka Leitungswasser bei 18.9°C. bestimmt. Die Dichtmessungen führten wir

(1) E. H. Ingold, C. K. Ingold, H. Whitaker, und R. Whytlaw-Gray, *Nature*, **134** (1934), 661; H. L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484; Vgl. auch L. A. Webster, M. H. Wahl, und H. C. Urey, *J. Chem. Phys.*, **3** (1935), 129.

mittels eines Quarzschwimmers durch. Die Messgenauigkeit dürfte $\pm 0.5\ \gamma$ sein.

Wir haben zwei Reihen von fraktionierten Elektrolysen durchgeführt. Bei der ersten, ausgegangen von 10 l. Osaka Leitungswasser, wiederholten wir die Elektrolyse dreimal und bei der anderen, angefangen mit 5 l. originalem Wasser, wurden die sukzessiven Elektrolysen fünfmal nacheinander durchgeführt. Aus diesen Versuchen hat sich ergeben, dass das spezifische Gewicht des rekombinierten Wassers nach der dritten Stufe der Elektrolyse unabhängig von der Zahl der Elektrolysen fast konstant geworden ist.[2] Das spezifische Gewicht des rekombinierten Wassers nach der dritten Stufe der Elektrolyse erwies sich durchschnittlich um $19.3\ \gamma$ leichter als das des Osaka Leitungswassers. Nimmt man an, dass diese Differenz im spezifischen Gewicht allein von der Befreiung vom Deuterium herkommt, dann ergibt sich aus dem bekannten spezifischen Gewicht des reinen schweren Wassers, dass D/H Verhältnis im Osaka Leitungswasser $1 : 5500 \pm 200$ ist.

Die ausführliche Mitteilung der vorliegenden Arbeit wird später in diesem Bulletin erfolgen.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
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(2) Neuerdings hat Johnston (*loc. cit.*) ein leichtes Wasser durch sukzessive Elektrolysen des Columbus City Wasser hergestellt. Aber dabei hat er gefunden, dass die Dichte des rekombinierten Wassers immer wieder abnahm, sogar nach vermuteter vollkommenen Befreiung vom Deuterium. Dies hat er auf die elektrolytische Trennung der Sauerstoffisotope zurückgeführt. In unserem Fall haben wir keine solche stetige Abnahme der Dichte des rekombinierten Wassers gefunden. Die Erklärung für diese Diskrepanz kann man vielleicht in der Verschiedenheit der Versuchsbedingungen besonders der Rekombinationsanordnungen finden.

ISOTOPENZUSAMMENSETZUNG DES WASSERS AUS PETROLEUMQUELLEN.

(Vorläufige Mitteilung.)

Von Kenzo OKABE und Toshizo TITANI.

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Bei dem Versuch von A. F. Scott[1] wurde gefunden, dass das Wasser aus zwei amerikanischen Petroleumquellen von 5000 Fuss Tiefe innerhalb der Messgenauigkeit ($\pm 2\,\gamma$) dieselbe Dichte wie gewöhnliches Wasser der Erdoberfläche besitzt.

Wir haben das Wasser aus zehn japanischen Petroleumquellen, deren Tiefe zwischen 30 m. und 1500 m. lag, geprüft. Das Wasser wurde sorgfältig gereinigt und dessen spezifisches Gewicht im Verhältnis zu ebensogut gereinigtem Osaka Leitungswasser bei 21.0°C. mittels eines Quarzschwimmers gemessen. Die Messgenauigkeit war $\pm 0.5\,\gamma$. Aus dem Versuch ergab sich, dass das Wasser aus Petroleumquellen innerhalb der Messgenauigkeit meistens dieselbe Dichte wie gewöhnliches Wasser besitzt. Aber in einigen Fällen fanden wir einen kleinen aber untrüglichen Unterschied zwischen beiden Dichten. Zwei Proben aus Petroleumquellen, die je 833 m. und 754 m. Tiefe besitzen und zu derselben Erdschicht gehören, erwiesen sich um $1.6\,\gamma$ bzw. $1.9\,\gamma$ schwerer als Normalwasser. Eine andere Probe aus einer 30 m. tiefen Bohrung erwies sich dagegen um $1.5\,\gamma$ leichter als gewöhnliches Wasser. Daher liegt die Vermutung nahe, dass nicht die Tiefe der Bohrungen sondern die Erdbeschaffenheit dabei eine Rolle spielte.

Die ausführliche Publikation wird später in diesem Bulletin erfolgen.

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und
Schiomi Institut für Physikalische
und Chemische Forschungen.

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(1) A. F. Scott, *Science*, **79** (1934), 565; vgl. auch H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell and H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1948.

DIE WIRKUNG DES VERDÜNNTEN SCHWEREN WASSERS AUF DIE TUBERKELBAZILLEN.[1]

Von M. ITOH, K. INOSHITA und T. TITANI.

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Über die biologische Wirkung des schweren Wassers in grossen Verdünnungen sind schon viele Versuche ausgeführt worden. Dabei hat sich in einigen Fällen ergeben,[2] dass das verdünnte schwere Wasser auf kleine Lebewesen günstig wirkte. Angeregt durch diese Entdeckungen untersuchten wir die Wirkung des verdünnten schweren Wassers auf das Wachstum der Tuberkelbazillen.

Zwei Stämme von Tuberkelbazillen, einer vom Typus bobinus und der andere vom Typus humanus Kamiike, wurden auf dem Longschen Nährboden kultiviert. Der Nährboden wurde auf die übliche Weise aus gewöhnlichem sowie verdünntem schweren Wasser, das je 0.08, 0.37 und 2.24 atomprozentiges Deuterium enthielt, dargestellt. Ausserdem liessen wir auch die Wasserstoffionenkonzentration der Nährlösung von *p*H 7.25 bis 5.83 varieren. Auf diese Weise wurden die Bakterien auf eine Serie von Nährböden, die in bezug auf Deuterium- sowie Wasserstoffionenkonzentration untereinander verschieden waren, schwimmkultiviert. Nach bestimmten Tagen verglichen wir den Grad des Wachstums der Bakterien auf jedem Nährboden durch die Grösse der Kolonie untereinander. Aus diesem Versuch ging ziemlich eindeutig hervor, dass die Zunahme der Wasserstoffionenkonzentration hemmend, dagegen die Zunahme der Konzentration des Deuteriums fördernd auf das Wachstum der beiden genannten Bakterien wirkte.

Herrn Prof. Dr. Imamura als Direktor des Takeo Instituts sind wir zum besten Dank verpflichtet.

Takeo Institut für Tuberkulosenforschung,
Schiomi Institut für Physikalische
und Chemische Forschungen
und
Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka.

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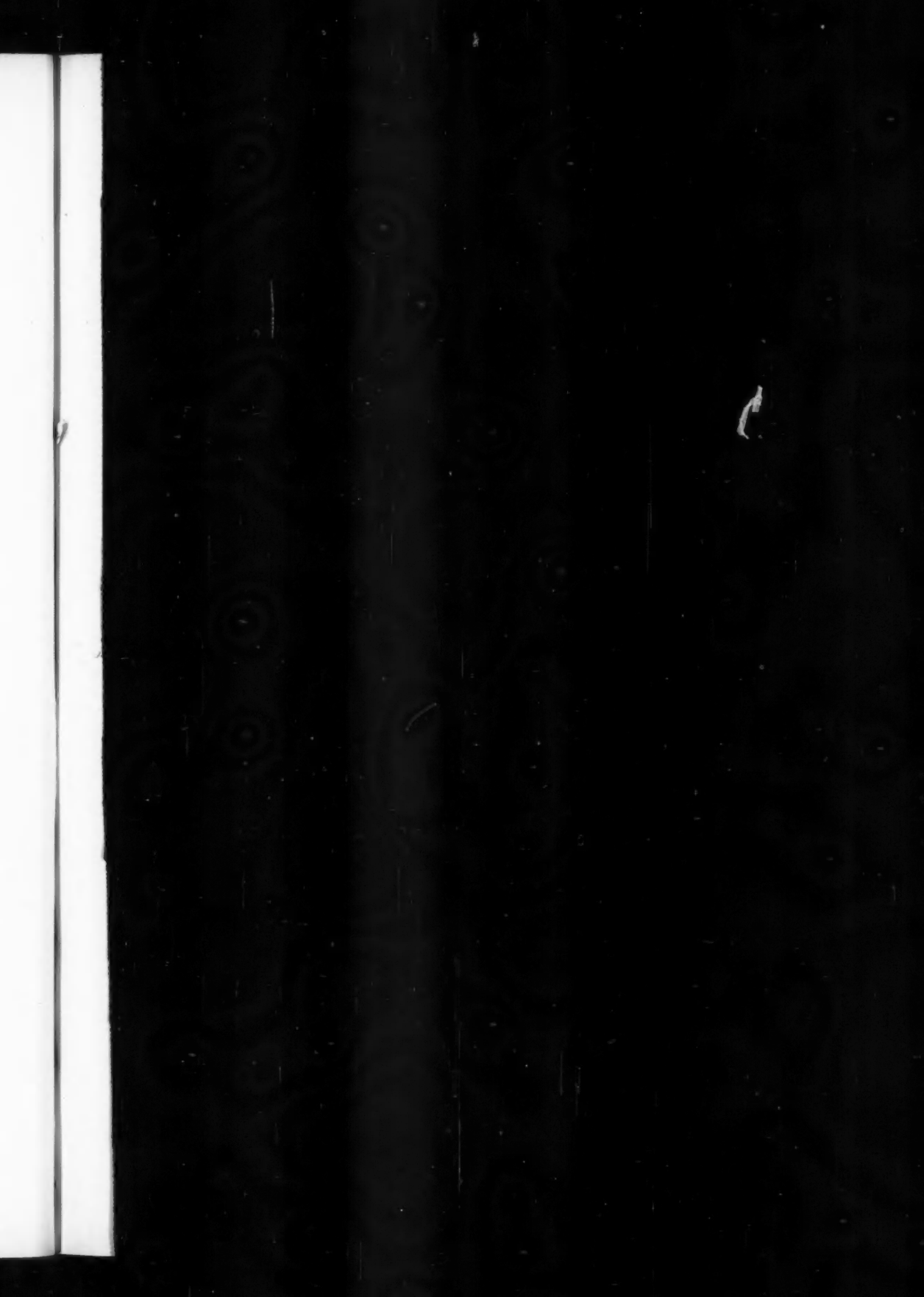
(1) Auszug aus der deutschen Mitteilung im "*Osaka Ijishinshi*", **6** (1935), Juni.

(2) S. L. Meyer, *Science*, **79** (1934), 210; T. C. Barnes, *J. Am. Chem. Soc.*, **55** (1933), 4332, *Science*, **79** (1934), 370; E. J. Larson und T. C. Barnes, *Nature*, **133** (1934), 873; T. C. Barnes und E. J. Larson, *Protoplasma*, **22** (1934), 431; G. Lockmann und H. Leunig, *Ber.*, **67** (1934), 1299; O. W. Richards, *J. Bact.*, **28** (1934), 289.